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QUALITATIVE
ORGANIC ANALYSIS

QUALITATIVE ORGANIC ANALYSIS

An Elementary Course in the Identification of Organic Compounds

BY

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PREFACE

THE teaching of Qualitative Organic Analysis is gradually receiving recognition as an important factor in the training of the chemist. In 1905, the subject was taught in only two or three universities; ten years later courses were offered in from fifteen to twenty of the leading schools in this country; and in 1918 the subject was prescribed for all colleges undertaking the training of chemists under the supervision of the United States Government. Only the armistice prevented the institution of this sweeping innovation in chemical curricula.

Qualitative Organic Analysis has not been taught generally because of the assumption on the part of chemists that the multiplicity of organic compounds excludes the possibility of a systematic procedure. This is the opinion of those who have not taught the subject; those who have had experience in presenting the work both in the classroom and the laboratory realize that Qualitative Organic Analysis is capable of logical and systematic treatment and that it is of fundamental importance in the elementary training of the chemist in the organic field.

The course here outlined is essentially that offered by the writer at the University of Illinois in 1920. The basis for its claim to systematization is outlined in Chapters I and II. The most radical individual departure from other analytical schemes consists in the subdivision of organic compounds into seven solubility groups and the application of this classification to a systematic procedure.

The chemist to whom most credit is due for the development of organic qualitative analysis is Professor S. P. Mulliken. The appearance of his exhaustive reference book on the "Identification of Pure Organic Compounds," Vol. I, in 1905 is obviously the beginning of this line of work. The authors of foreign texts

on the subject have curiously avoided crediting the pioneer in the field. The present writer extends such recognition with pleasure. He wishes also to offer hearty acknowledgment to his teacher and colleague, Dr. C. G. Derick, at whose suggestion the presentation of this text was undertaken. The procedure here outlined is based upon a course offered by Dr. Derick in 1908 and subsequently developed with his constant sympathetic help and encouragement during the years 1911–1915.

The course outlined in this text is intended to follow the usual work in synthetic organic preparations; Part A corresponds to the classroom work, while Part B embodies the actual laboratory directions. The steps required in the identification of an unknown are outlined in Chapter VI and are treated in more detail in the subsequent chapters in the order in which they are required in an actual identification. The work is usually apportioned as follows for a one-semester course of sixteen weeks, covering thirty-two laboratory periods of three hours each.

Solubility Tests on Known Compounds,
Chapter VIII. One week.

Classification Reactions on Known Compounds,
Chapter IX. Five weeks.

Identification of Six or Eight Individual Compounds,
Chapters VI–XI. Six weeks.

Examination of Mixtures,
Chapter XII. Four weeks.

In certain branches of study, and particularly in Chemical Engineering, the schedule will not permit instruction in Qualitative Organic Analysis as a separate course. In such classes it has been found best, nevertheless, to present an abbreviated six or eight weeks' course in place of the latter part of the second semester's work in organic synthesis. Such an abbreviated course should consist of the solubility work of Chapter VIII, selections from Chapter IX so as to require only about three weeks' work, and the identification of about four individual compounds.

The classified tables in Part C have not previously been used in actual laboratory instruction and suggestions in regard to corrections and additions from those who have occasion to use them in classwork will be appreciated. The tables are intended only for preliminary aid before resorting to the advanced reference books. Formulas and specific instructions for the choice of deriva-

tives are omitted for pedagogical reasons; the former are usually superfluous and the latter should be a part of the student's own work based upon the principles discussed in Chapter X.

The writer takes this opportunity to acknowledge his indebtedness not only to the extensive works by Mulliken, but also to the authors of two smaller but nevertheless very valuable manuals that have from time to time been used as text-books in his courses, namely: Clarke's "Handbook of Organic Analysis" and Noyes and Mulliken's "Laboratory Experiments on the Class Reactions of Organic Substances (1897)." He also wishes to express his gratitude to Dr. C. S. Marvel, who has read the manuscript and offered other valuable assistance, to Dr. E. A. Wildman, who has read the proof, and to Mr. A. O. Matthews, who has prepared the drawings.

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DETROIT, MICHIGAN
October, 1922.

The hearty reception given to this elementary text has been gratifying indeed and its increasing use has necessitated several reprintings. Although it was estimated that courses in qualitative organic analysis were offered in only fifteen or twenty schools during 1915, ten years later even this little manual found a use in approximately one hundred universities and colleges.

Commercial research and business duties are scarcely compatible with the writing or revision of a text-book but in justice to the increasing number of users, a revision is now planned for January, 1930, and the writer will welcome suggestions concerning improvements to be incorporated.

DETROIT, MICHIGAN
May, 1929.

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QUALITATIVE ORGANIC ANALYSIS

PART A

CHAPTER I

THE METHOD OF QUALITATIVE ORGANIC ANALYSIS

The multiplicity of organic compounds, the instability of many of the individual members when compared with the more common inorganic compounds, and the relative complexity of mixtures of organic substances (particularly many of the mixtures obtained from natural products) make organic analysis appear difficult to the uninitiated. Inorganic analysis, on the other hand, appears simple and systematic because we have too arbitrarily limited it more or less to a method for the analysis of the commoner ions; no scheme has yet been proposed for a complete and systematic method for the analysis of *inorganic compounds.*

In the present procedure for qualitative organic analysis no attempt is made to outline for organic chemistry that which has not yet been accomplished in the older inorganic field; it is intended as an elementary introductory course to form a groundwork for the more specialized lines of advanced organic analysis, many of which still lie mainly in the realm of research.

In discussing the procedure for the identification of an organic compound, it is well for us to differentiate between (*a*) the method of characterizing new organic compounds which

have not been described previously and (*b*) the more rapid method that may be applied to those compounds which have already been subjected to characterization. It will be found, however, that the qualitative procedure often will be applicable even to the identification of compounds not yet described in the literature.

THE CHARACTERIZATION OF AN ORGANIC COMPOUND

When a new compound is prepared in the laboratory or when a new individual is isolated from some natural source, extensive work is often required for the complete assignment of its structure; i.e., for the characterization of the compound. The usual steps in the procedure for the assignment of structure to both organic and inorganic compounds are as follows:

(1) Isolation and Purification,
(2) Qualitative Analysis,
(3) Quantitative Analysis,
(4) Molecular Weight Determination.

These four steps are often sufficient for the characterization of an inorganic compound; on the other hand, organic compounds almost invariably require a fifth consideration:

(5) Assignment of Structure According to the Atomic Linking Theory,
  (*a*) Analytical Method of Structure Proof,
  (*b*) Synthetical Method of Structure Proof.

The importance of the last step may be illustrated best by a specific example. A definite chemical individual is isolated from a natural product. Qualitative analysis demonstrates the presence of carbon, hydrogen, and oxygen. Quantitative analysis shows these three elements to be present in the proportions

$$2C : 4H : 1O.$$

The formula for the compound can therefore be written $(C_2H_4O)_x$. Molecular weight determinations demonstrate the value of x to

be three; the correct molecular formula can now be adopted as $C_6H_{12}O_3$. A glance at the literature shows, however, that this formula represents the true composition of about eighty organic compounds; obviously then these compounds possess different internal structures and it is necessary to ask the question, "How are the atoms arranged within the molecule?" It is by answering this question that we can differentiate between these various isomers, and this answer is obtained by applying in the aid of the Atomic Linking Theory the analytical and synthetical methods for structure proof.

If the procedure outlined above were the one actually used in a laboratory course in qualitative organic analysis, the identification of an organic compound would be a very difficult and laborious task indeed. It is fortunate, therefore, that a simpler method is at hand.

In connection with the identification of an organic compound, time will usually not permit a quantitative analysis for the elements (step three, above), since it is desired to identify a compound not in a few days' time, but during a few hours. For the same reason, molecular weight determinations are applied only in exceptional instances. Step five, the assignment of structure, often involves years of investigational work. Fortunately, this work has already been accomplished for an enormous number of organic compounds, and the path has thus been cleared in the direction of qualitative identification when these compounds are again met.

THE METHOD OF SUPERPOSITION

A given unknown organic compound is said to be identical with a known when the two compounds agree perfectly in all of their physical and chemical properties. Such a method is of course impractical, and actual laboratory experience teaches us that agreement between several of the physical properties together with uniformity of the chemical reactions of the two compounds,[1] justifies us in assuming complete agreement in all properties either physical or chemical.

[1] This implies also that the products of the reactions (derivatives) must agree in their physical constants.

The method of superposition lies at the basis of any scheme of identification, but because of the multiplicity of organic compounds this method in itself would prove of little value; a scheme of analysis dependent upon it alone would lead to an immense amount of unnecessary work without the equivalent return in development of logical thinking and without the accumulation of a systematic knowledge of organic chemistry which may be best developed in the qualitative field. In order to be of value, the method of superposition must be preceded by a systematic method of elimination.

THE METHOD OF QUALITATIVE ORGANIC ANALYSIS

The steps to be taken in the rapid identification of a compound which has previously been characterized are as follows:

1. Purification of the compound and determination of the most common physical constants,
2. Qualitative analysis for the elements,
3. Determination of solubility behavior,
4. Application of class reactions to those types indicated by tests 1, 2, and 3,
5. Use of the literature on known classes of compounds,
6. Preparation of derivatives and determination of physical constants of these derivatives.

The systematic method for the identification consists in locating first *not the individual compound but the class or preferably the homologous series to which the compound belongs.*

Let the student be given an unknown organic compound, which may be any one from among thousands of known compounds. Obviously, it would be a waste of time to search through the literature in order to find constants and reactions of known compounds which check with the physical and chemical properties of the unknown. We shall seek first the "class" to which the unknown belongs. The determination of its melting- or boiling-point will exclude certain classes of compounds; the qualitative analysis for the elements (C, H, N, S, X, etc.), will further limit the possible classes, and after the application

of the prescribed solubility tests the possibilities will be still more limited. Furthermore, the "class reactions," the so-called homologous tests, will limit the number of classes to very few, and preferably to only one. At this stage, *but not before*, may the literature be consulted. The position of the compound within a given class will then be determined by means of its physical constants, and to prove absolutely that the process of reasoning is correct, as well as to differentiate between several possible individuals, one or more derivatives are prepared and identified by means of their physical constants.

THE THEORETICAL BASIS FOR QUALITATIVE ORGANIC ANALYSIS

The Value of Homology.—In the procedure for qualitative identification of an unknown, as sketched above, systematization is possible because of the occurrence of homology. Fortunately, nature has divided the immense number of organic compounds into certain definite series called homologous series. In an homologous series a given member differs from the preceding or succeeding member by the constant difference, CH_2. For example, in the homologous series comprising the monobasic paraffin acids, we have as the first five members:

HCO_2H	Formic acid,
CH_3CO_2H	Acetic acid,
$CH_3CH_2CO_2H$	Propionic acid,
$CH_3CH_2CH_2CO_2H$	Butyric acid,
$CH_3CH_2CH_2CH_2CO_2H$	Valeric acid, etc.

From a scientific standpoint, the existence of homology is of fundamental importance for two reasons: (1) The chemical properties of every member of an homologous series are the same; they differ only in the *speed of reaction, not in the kind of reaction.* (2) The physical properties of the members of a given homologous series are different. For example, in the above homologous series we note in each member the presence of a carboxyl group together with a saturated radical, hence each acid must possess the chemical properties of these two radicals, i.e., must possess the same chemi-

cal properties. (We note, however, that in the above series, the first member possesses a carboxyl group united to a hydrogen atom and we may expect therefore a variation in certain chemical properties.) On the other hand, each member of a given homologous series may be differentiated from any other member by means of physical properties.

TABLE I

Name	M. p.	B. p.	Sp. gr. 25°/25°	M. p. of *p*-toluidide	M. p. of *p*-nitrobenzyl ester	Duclaux constant
Formic acid.....	+ 8°	101°	1.291	52°	31°	4
Acetic acid.....	+15°	118°	1.051	153°	78°	7
Propionic acid....	−22°	141°	0.991	123°	31°	11
n-Butyric acid....	− 8°	162°	0.956	74°	35°	18
Isobutyric acid....	− 5°	155°	0.946	109°	liquid	25
n-Valeric acid.....	−58°	185°	0.937	70°	....	28

The homologous series to which the unknown compound belongs must be determined mainly by means of the chemical reactions characteristic of its groups and then its physical properties will reveal the position of the compound in the homologous series. The principle of homology has been kept in mind in outlining the method of analysis given above. In actual practice, it is found more convenient to consider *classes* of organic compounds in place of homologous series. In some instances these classes may be identical with given homologous series, whereas in other cases a class may comprise members from several homologous series; for instance, under primary aromatic amines we shall classify aniline, α-naphthyl amine, *o*-anisidine, *p*-aminoacetophenone, etc. Although each one of these four individuals belongs to a different homologous series, they all exhibit analogous chemical reactions in respect to the amine group.

In the subsequent laboratory work, we shall seek to apply the systematic procedure outlined above under "The Method of Qualitative Organic Analysis."

REFERENCES

The following books are suggested for reference in connection with the study of Qualitative Organic Analysis: Mulliken, The Identification of Pure Organic Compounds, Vols. I, II, III, and IV; Rosenthaler, Nachweis Organischen Verbindungen; Clarke, Handbook of Organic Analysis; Weyl, Methoden der Organischen Chemie; Allen, Commercial Organic Analysis; and Sherman, Organic Analysis (Foods).

The student, from his previous training in organic chemistry, is expected to be familiar with reference books such as Richter's Lexicon and Beilstein's Handbuch, and he should cultivate a familiarity with Chemical Abstracts as a source for the more recent work. For specialized subjects the references on pp. 105–106 may be consulted.

CHAPTER II

THE SOLUBILITY BEHAVIOR OF ORGANIC COMPOUNDS

Physical Properties and Molecular Structure.—The atomic linking theory attempts to explain the physical and chemical properties of organic compounds by means of the linking together of atoms. In applying the theory for the prediction of the physical properties of organic compounds, the following considerations are of fundamental significance:

(*a*) The kind and number of atoms present (chemical composition),
(*b*) The mode of linking of the atoms (constitution),
(*c*) The spatial arrangement of the atoms (configuration).

In any systematic method for the identification of organic compounds, both physical and chemical properties are utilized for locating the class, or, preferably, the homologous series to which the unknown belongs, and subsequently specific physical tests are applied to locate the individual within the series. Unfortunately for organic analysis, the study of the relationship between physical properties and molecular structure is still a relatively undeveloped field, certainly so when viewed from the standpoint of potential possibilities.

In the present chapter, we shall discuss in an elementary manner the relation to molecular structure of only one physical property, that of solubility. This topic is chosen because it lies at the basis of the present scheme of analysis. The discussion is intended for the beginner; the experienced analyst is able to utilize efficiently generalizations based upon other physical properties as well.

Prediction of Solubility.—From the atomic linking structure of an organic compound, we may with fair assurance predict in

a qualitative way its solubility behavior. For the purposes of qualitative organic analysis we may reverse this procedure, and from the results of solubility tests draw certain inferences concerning the nature of a given unknown; these will depend upon the results of an elementary analysis of the compound as well as upon its physical constants. It is for this reason that qualitative analysis for the elements and a determination of the physical constants should precede conclusions drawn from the solubility behavior of a given compound.

Arbitrary Classification of Solvents.—In discussing the solubility behavior of organic compounds, we shall for convenience place the solvents used in two groups:

(*a*) Inert solvents,
(*b*) Reaction solvents.

This division, we shall find, is not altogether sharp. Under Inert Solvents we shall arbitrarily group those solvents, like water, ether, alcohol, benzene, etc., which may be predicted to exert their solubility effects because of a structural relationship to the substance dissolved.

Under Reaction Solvents we shall group those solvents which cause solubility because of a chemical reaction of the kind ordinarily expressed by equations; viz., the neutralization of an acid by a base with the production of a soluble salt. The fact that solubility in water may produce ionization or hydrolysis in certain cases and solvation in general is recognized, but nevertheless an arbitrary distinction of this kind will prove of value in the subsequent discussion.

RULES FOR THE PREDICTION OF SOLUBILITIES IN THE INERT SOLVENTS

For the prediction of the solubilities of organic compounds in the Inert Solvents we shall have occasion to apply four fairly general rules:

I. A substance is most soluble in that solvent which is most closely related structurally to the solute.
II. As we go higher in a given homologous series, the members become more and more, in their *physical*

properties, like the hydrocarbons from which they may be considered as being derived.

III. Compounds of very high molecular weight, such as highly polymerized compounds, exhibit decreased solubility in the inert solvents.

IV. The solubility behavior of solid compounds is dependent upon the molecular aggregation in the solid state.

The four solubility rules have been presented in the order given for the reason that in the prediction of the solubility behavior of a known compound they will be used in this order. Knowing the formula for a given compound, we proceed first to predict its solubility in a special solvent on the basis of relationship in structure between the solute and the solvent. (Rule I.) Next, we must consider the effect of position within the homologous series (Rule II) and for this purpose we must be able to predict, of course, the solubility behavior of the hydrocarbons. Finally, we must consider possible limitations imposed by the two qualifying Rules III and IV.

Discussion of the Rules of Solubility.—Rule I. *A substance is most soluble in that solvent which is most closely related structurally to the solute.* This rule will receive verification from the elementary applications that will be presented throughout this chapter. Hexane is insoluble in water (1 : 1000), which is in accordance with what we should expect from the dissimilarity in structure between hydrocarbons and water. On the other hand, hexane dissolves in three parts of methyl alcohol, while in ethyl alcohol it is soluble in all proportions; ethyl alcohol is closely enough related to hexane in structure to produce miscibility. Naturally we shall not hesitate, therefore, to predict that hexane will dissolve in all proportions in a very intimately related solvent, octane; in fact, such a mixture will give rise to what the physical chemist terms " an ideal solution " since it obeys the same laws that ordinarily apply only to extremely dilute solutions.

Although ethyl alcohol and hexane dissolve in all proportions and although this relationship holds for many of the homologues not only of the series C_nH_{2n+2} but also for the series C_nH_{2n}, C_nH_{2n-6}, etc., we find that paraffin hydrocarbons of sufficiently high molecular weight are not completely miscible in ethyl alcohol; for

example, ordinary kerosene requires several volumes of ethyl alcohol for complete solution. This behavior is covered by Rule III. Although kerosene is not completely miscible in ethyl alcohol, we may predict, according to Rule I, that it will dissolve more readily in an alcohol of higher molecular weight (butyl alcohol), which is more closely related to kerosene in composition. Actual experiment verifies this prediction.

A few additional specific examples dealing with some common organic compounds will be presented here to illustrate the application of Rule I.

TABLE II

SOLUBILITY OF *p*-DIBROMOBENZENE IN VARIOUS SOLVENTS AT 50°

Solvent	Grams solute per 100 grams of saturated solution	Solvent	Grams solute per 100 grams of saturated solution
HOH	0.0	$C_2H_5OC_2H_5$	67
CH_3OH	20	CS_2	72
CH_3CH_2OH	26	C_6H_6	71
$CH_3CH_2CH_2OH$	27	C_6H_5Br	54
$(CH_3)_2CHCH_2OH$	30		

The effect of substitution in organic compounds by halogen usually results in decreased solubility in the inert solvents; the effect of halogen is therefore analogous to an increase in number of carbon atoms. *p*-Dibromobenzene is insoluble in water, but is extremely soluble in a solvent like benzene, which is closely related in structure to the solute. The alcohols lie intermediate in structure between water and the hydrocarbon solvents, and this corresponding effect is reflected in the data of Table II. Ether is still more closely related to the hydrocarbons and the above solubility value is such as might be predicted qualitatively. The solubility of *p*-dibromobenzene is less in bromobenzene than in an equal weight of benzene, but this irregularity is less serious when solubility is expressed in grams of solute per mole of solvent. The result exhibited by carbon disulfide may appear like an exception until the information on page 12 is considered.

TABLE III

Solubility of Naphthalene in Various Solvents at 20°

Solvent	Grams naphthalene per 100 grams solvent	Solvent	Grams naphthalene per 100 grams solvent
HOH	0.003	$CH_3CH_2CH_2CO_2H$	22
CH_3OH	8.2	$(CH_3)_2CHCH_2CO_2H$	17
CH_3CH_2OH	9.8	$CHCl_3$	31
$CH_3CH_2CH_2CH_2CH_2CH_3$	14.0	CS_2	36
CH_3CO_2H	13.0	C_6H_6	36
$CH_3CH_2CO_2H$	23	$C_6H_5CH_3$	28

Problem 1.—Interpret the data in Table III in accordance with predictions based upon Rule I. Why would the solubility of naphthalene in mono-hydroxy alcohols up to C_6 be predicted to lie below 14 g. per 100 g. solvent? Given the solubility in acetic acid, do the solubilities in propionic, butyric and valeric acids agree with predictions? Why would one expect naphthalene to be less soluble in toluene than in benzene? Predict qualitatively the solubility of naphthalene in the solvents formic acid, heptanoic acid, ethyl benzene, etc. Compare the solubilities in hydrocarbons of the two series C_nH_{2n+2} and C_nH_{2n-6}, where $n = 6$. Do the facts agree with predictions? Predict qualitatively the solubility of naphthalene in ethyl acetate.

Prediction of solubility in the inert solvents such as carbon disulfide, carbon tetrachloride, chloroform, etc., is somewhat more difficult. In these instances it is sometimes convenient to consult the following table of dielectric constants. No definite relationship between dielectric constants and solubilities has been developed since unknown factors are involved; nevertheless, the dielectric constants may be used where they do not conflict with the more basic generalization given in Rule I.

TABLE IV

Dielectric Constants of Some Organic Solvents at 18° to 20°

Water	81	Ethyl acetate	6.5
Methyl alcohol	32	Bromobenzene	5.2
Ethyl alcohol	26	Chloroform	5.2
Propyl alcohol	22	Ethyl ether	4.4
Isobutyl alcohol	19	Carbon disulfide	2.6
Isoamyl alcohol	16	Benzene	2.3
Ethyl bromide	10	Carbon tetrachloride	2.25
Acetic acid	9.7	Hexane	2.0

According to Rule I, we may predict that naphthalene will dissolve to a limited extent in either ethyl alcohol or glacial acetic acid. A selection of the most efficient of these two solvents would be difficult without actual experiment. The dielectric values, however, indicate that acetic acid will prove superior. Explain. On the other hand, benzene and hexane differ only slightly in dielectric constants. Since benzene is very much more closely related in structure to naphthalene than is hexane, we find that the solubility of naphthalene is considerably greater in the former solvent: Rule I takes precedence over predictions based upon dielectric constants.

Problem 2.—Look up in Seidell, "Solubilities of Inorganic and Organic Compounds," 1919, p. 136, the solubility of benzoic acid in various organic solvents. Compare these values with the corresponding dielectric constants.

Although the two common solvents, chloroform and carbon tetrachloride, are very closely related in composition, the table of dielectric constants suggests considerable variation in the solvent powers of these two compounds, which prediction is in agreement with actual experience. In many instances, chloroform exhibits an unusual solvent power. This is especially noticeable in the solubilities of some of the well-known alkaloids, such as atropine, quinine, cinchonine, quinidine, and hyoscyamine.

The Second Rule of Solubility.—*As we go higher in a given homologous series, the members become more and more, in their physical properties, like the hydrocarbons from which they may be considered as being derived.* It should be noted that this statement is very broad in its application; it refers to physical properties in general, whereas in our discussion we require only a limited application to one physical property, that of solubility in the inert solvents.

Figure 1 illustrates the application of the rule to the solubility in water of the aliphatic mono-hydroxy alcohols and monocarboxylic acids. Beyond the members possessing five carbon atoms the solubilities of the oxygenated derivatives rapidly approach those of the hydrocarbons.

Many other illustrations of Rule II, together with numerical data, will be discussed in the latter part of this chapter in connection with the development of the solubility table.

The Third Rule of Solubility.—*Compounds of very high molecular weight exhibit decreased solubility in the inert solvents.* This is true even when the solvent and the solute are in the same homologous series, provided that there is sufficient difference in molecular weight. For example, low-boiling ligroin will not dissolve solid paraffin in all proportions. Similarly, acetic acid will dissolve stearic acid only to the extent of about 5 per cent at 20°.

The formula $C_6H_{12}O_6$ immediately suggests a sugar very soluble in water, but $(C_6H_{10}O_5)_x$ may represent a water-insoluble substance like cellulose. CH_2O and $CH_3-C(=O)-H$ represent compounds extremely soluble in water, whereas $(CH_2O)_x$ and $(CH_3-C(=O)-H)_3$ represent substances of limited solubility in water.

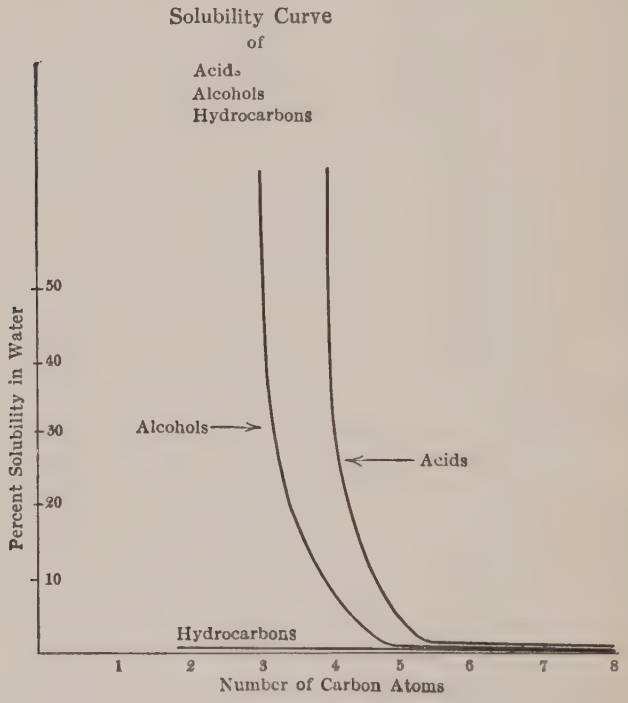


Fig. 1.

From the reaction between an amine and an organic acid we may isolate an amide of normal solubility. When, however, a diamine, such as *p*-phenylene diamine or benzidine, reacts with a dicarboxylic acid, the primary reaction-product may react again and again to yield finally substances of very high molecular weight. Such products are insoluble in the inert solvents. Many other analogous instances might be cited. Among the substances of high molecular weight we must make allowance, however, for

certain types that yield colloidal solutions; this is especially noticeable with certain starches, proteins, and dyes.

The Fourth Rule of Solubility.—*The solubility behavior of solid compounds is dependent upon the molecular aggregation in the solid state.* It is because of this factor that the solubility behavior of liquid compounds may be predicted more safely than that of solids. Solubility is dependent upon the species in equilibrium with the saturated solution. The molecular aggregation in the solid state finds expression, however, in other physical properties; for example, in the melting-points of the compounds. By judicious use of relationships which have been pointed out in this field, we possess a means of predicting many cases of solubility that might otherwise be treated as exceptions.

Among compounds of a given homologous series, high melting-points[1] may often be associated with low solubility. Among isomeric substances (space isomerism) the isomer least stable toward rearrangement possesses the lowest melting-point and the greatest solubility. Among position-isomers, such as the isomeric di- and tri-substitution products of benzene, only a fair agreement is found, with the assumption that the solubilities of the isomers are in the order of their melting-points.[2]

The melting-point and solubility relationships of the saturated aliphatic dicarboxylic acids illustrate this rule (IV) among compounds that are not isomeric but homologous. In this series, we must apply Rule II separately to the acids with odd and to those with even numbers of carbon atoms. Beyond the C_7 member, we find, however, that one group is rapidly approaching the solubility of the other and both groups are rapidly approaching the solubilities of the corresponding hydrocarbons. (See Fig. 2.)

In agreement with Rule IV, we find that the solubility of an organic compound is greater when the saturated solution is in equilibrium with the liquid substance than when in contact with the solid at the same temperature. For example, at 70° benzoic acid is soluble in water to the extent of 2 per cent provided that the saturated solution is in contact with solid benzoic acid; when

[1] This does not apply to compounds of the "salt type."

[2] Carnelley and Tomson, J. Chem. Soc. **53**, 791 (1888); **73**, 618 (1898); J. prakt. Chem. **52**, 72 (1895); **59**, 30–45 (1899); J. Chem. Soc. Abstracts **92**, i, 745 (1907).

in contact with liquid benzoic acid the solubility is three times as large.

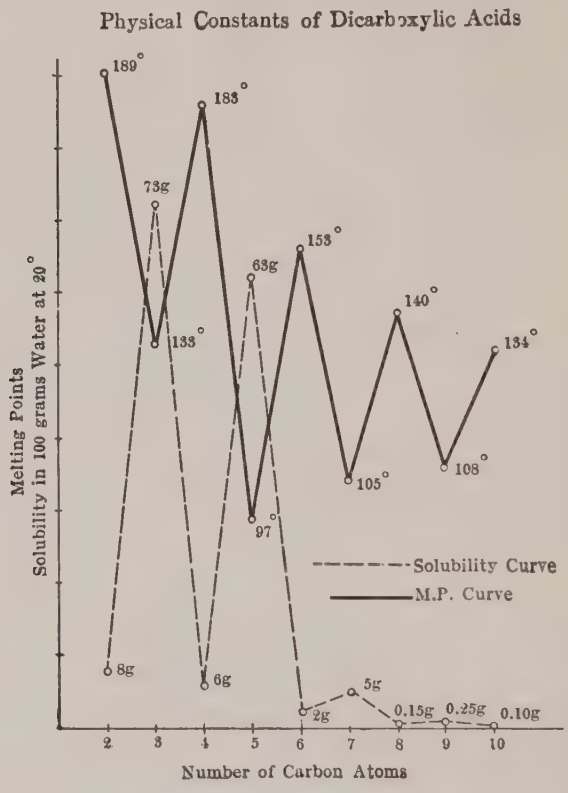


FIG. 2.

A number of other well-known examples will now be considered. Among geometrical isomers (cis-trans type) we find that the most fusible isomer possesses also the greatest solubility. (See Table V.)

A case analogous with the above is that dealing with the various isomeric cinnamic acids. The ordinary stable isomer (m. p. 133°) is soluble in water at 25° to the extent of about one part in 15,000 while the labile acids (m. p. 68°, 58°, 42°) are soluble in about 100 parts of water.

Among optical isomers, dextro and laevo enantiomorphs possess identical melting-points and identical solubilities. The racemic form usually differs in melting-point and in solubility. Among

this class of compounds we find many examples illustrating the fact that solubility depends upon the molecular complexity of the solid. The tartaric acids furnish a typical illustration.

In solution, the racemic tartaric acid may be represented as $CO_2H \cdot (CHOH)_2 \cdot CO_2H$, as is indicated by its cryoscopic depression and its ionization constant; its solubility is controlled, however, by the molecular complexity of the solid. (See Table VI.)

TABLE V

Substance	M. p.	Solubility in 100 grams solvent at 20°.	
		Water	Ethanol
$CH—CO_2H$ $\|\|$ maleic acid ..... $CH—CO_2H$	130°	60 g.	51 g.
$HC—CO_2H$ $\|\|$ fumaric acid..... $CO_2H—CH$	286° subl.	0.6 g.	5 g.

TABLE VI

	M. p.	Solubility in 100 g. water (20°)	Solubility in 100 g. alcohol (25°)
$C_4H_6O_6$ *d*-tartaric acid.....	170°	139 g.	27 g.
$C_4H_6O_6$ *l*-tartaric aicd.....	170°	139 g.	27 g.
$(C_4H_6O_6 \cdot H_2O)_2$ *dl*-tartaric acid... (racemic)	205–206°	20.6 g.	2 g.

Among the di- substituted benzene derivatives, we find very often that the order of solubility lies in the order of the melting-points. This is illustrated in the solubilities of the following substituted benzoic acids.

TABLE VII

Name of acid	Melting-point of acids			Solubility in 1000 grams of water at about 25°		
	Ortho	Meta	Para	Ortho	Meta	Para
Chlorobenzoic	142°	158°	243°	2.25	0.45	0.09
Bromobenzoic	150°	155°	254°	1.86	0.40	0.056
Iodobenzoic	162°	186°	265°	0.95	0.12	0.027
Toluic	104°	110°	179°	1.18	0.98	0.35
Phthalic	230°	300°	Subl.	10.	0.13	0.0
Nitrobenzoic	147°	141°	238°	[7.4]	3.4	0.3
Hydroxybenzoic	158°	200°	213°	[2.5]	10.8	6.5
Aminobenzoic	144°	174°	187°	[3.4]	5.6	3.1

In comparing the meta and para compounds in Table VII, it will be noticed that the higher-melting isomers are also the less soluble in water. This rule cannot at present be made more general so as to include also the ortho isomers because a number of well-known exceptions exist; these exceptions are indicated in the table by the brackets. It appears probable, however, that this irregularity is mainly disposed of in a solvent like benzene, which is more closely related in structure to the solute. See Table VIII.

TABLE VIII

Name of compound	Melting-point			Per cent solubility at 20° in benzene		
	Ortho	Meta	Para	Ortho	Meta	Para
Hydroxybenzoic	158°	200°	210°	0.8	0.01	0.004
Nitrobenzoic	147°	141°	238°	0.4	1.0	0.03
Nitrophenol	44°	95°	114°	50.	1.5	0.5
Dinitrobenzene	118°	90°	173°	5.7	39	2.5
Nitraniline	69°	112°	148°	23	2.5	{0.6 2.0
Chloronitrobenzene	32°	44°	82°	70	48	29
Bromonitrobenzene	38°	53°	124°	60	35	5

SOLUBILITY IN THE REACTION SOLVENTS

For the purpose of classification, we shall find cold concentrated sulfuric acid an extremely valuable reagent; its main use consists in the subdivision of the group of compounds which we shall call the *indifferents*, i.e., compounds insoluble in water and containing neither acidic nor basic groups. We shall find that the saturated hydrocarbons (aliphatic and aromatic) are insoluble in this reagent *under the conditions of the experiment* and this holds true with but few exceptions chiefly among the tertiary members, for the halogen derivatives of these hydrocarbons. The oxygenated derivatives of these compounds (alcohols, ketones, esters, ethers, aldehydes, etc.) are almost invariably extremely soluble (occasionally with decomposition) in this solvent.

Cold concentrated sulfuric acid differs from the usual inert solvents mainly in that it forms a more stable addition product with the solute. The use of sulfuric acid in this solubility work is based not upon the usual sulfonation reactions but upon the formation of addition products from which the organic compound may usually be recovered unchanged. For example, ethyl benzoate will dissolve in all proportions in cold concentrated sulfuric acid to produce addition products[1] of the types

$$[C_6H_5CO_2C_2H_5 \cdot H_2SO_4] \quad \text{and} \quad [(C_6H_5CO_2C_2H_5)_2 \cdot H_2SO_4].$$

The ethyl benzoate may be recovered by pouring the acid solution into ice-water.

Basic Groups.—Compounds possessing basic groups will react with dilute hydrochloric acid to produce water-soluble hydrochlorides. Obviously, the degree of basicity of the amine group, the concentration of the acid used, and the solubilities of the amine salts are important factors, and these will be discussed in more detail in connection with the laboratory instructions.

By far the most common basic groups are the amino and certain substituted amino groups. Sulfonium hydroxides, certain oximes, pyrones and their naturally-occurring derivatives (the anthocyanins), represent basic compounds which need consideration only in more advanced work.

[1] J. Kendall, J. Am. Chem. Soc. **36**, 2498 (1914).

When an organic compound contains the group NH_2, it is not necessarily basic in nature; in fact it may be basic, neutral, or even acidic, the structure of that part of the molecule united to the NH_2 group exerting the controlling influence. When a hydrogen of ammonia is substituted by an *alkyl* or related radical, we obtain a primary amine which compares favorably with ammonia in basicity.

TABLE IX

	Ionization* constant $K_B^{25°}$		Ionization* constant $K_B^{25°}$
Ammonia	1.8×10^{-5}	Diethyl amine	1.26×10^{-3}
Ethyl amine	5.6×10^{-4}	Dimethyl amine	5.35×10^{-4}
Benzyl amine	1.95×10^{-5}	Triethyl amine	5.9×10^{-5}
Allyl amine	4.6×10^{-5}	Piperidine	1.2×10^{-3}

* Scudder: Conductivity and Ionization Constants of Organic Compounds (1914). The values are only apparent ionization constants for the reason that only a fraction of the amine is present as an ammonium compound. Cf. also Bredig, Zeit. Phys. Chem. **13**, 289–326 (1894).

When the second and third hydrogens of ammonia are replaced by alkyl radicals, we find that the resulting secondary and tertiary amines are of approximately the same order of basicity as the primary amines. (See second column of Table IX.)

If in place of alkyl or related radicals we introduce into ammonia an *aryl* radical, we note a tremendous drop in the ionization constant (Table X) to about one-millionth of its previous value. We may predict that a second radical, but of the alkyl type, will produce no further large change in basicity, but the introduction of a second aryl radical will produce a second large decrease in basicity, whereas a third aryl radical will produce a practically neutral substance. The phenomenon produced by two or three aryl groups may be accomplished by the introduction of a single radical of the *acyl* type. A second acyl radical will convert the nitrogen derivative into an acidic substance. That which is accomplished by means of two acyl groups may be called forth by a single group provided that the acyl group corresponds to a very strong acid (sulfonic acid). Examples of all of these cases are given in Table X.

TABLE X

Substance	Ionization constant	Reaction
$C_6H_5 \cdot NH_2$	$K_B^{25°} = 5 \times 10^{-10}$	Basic
$C_6H_5 \cdot NHCH_3$	$K_B^{18°} = 3 \times 10^{-10}$	Basic
$C_6H_5 \cdot N(CH_3)_2$	$K_B^{18°} = 3 \times 10^{-10}$	Basic
$(C_6H_5)_2NH$	.....	Almost neutral
$(C_6H_5)_3N$	.....	Neutral
$C_6H_5 \cdot CO \cdot NH_2$	.....	Practically neutral
$CH_3 \cdot CO \cdot NH_2$	$K_B^{25°} = 0.3 \times 10^{-14}$	Practically neutral
$CH_3 \cdot CO \cdot NH \cdot C_6H_5$	$K_B^{40°} = 4.0 \times 10^{-14}$	Practically neutral
$C_6H_4 \begin{matrix} \cdot CO \cdot \\ \cdot CO \cdot \end{matrix} NH$	$K_A^{25°} = 5 \times 10^{-9}$	Acidic
$C_6H_5 \cdot SO_2 \cdot NH_2$	.....	Acidic

Among the basic compounds we shall find therefore primary (I), secondary (II), and tertiary (III) amines, provided that not more than one of the substituting radicals is an aryl radical. The nitrogen may be part of a ring structure, as in pyridine and its derivatives. The quaternary ammonium bases, $(R)_4 \rightleftharpoons N—OH$, are very strong bases like the inorganic hydroxides, but they are usually met in the form of their neutral salts.

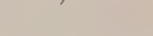
In addition to the basicity of the compound, we must consider also its solubility in water in order to predict its solubility in dilute aqueous hydrochloric acid. Amines of very high molecular weight occasionally possess such a slight solubility in water that they fail to dissolve in dilute acid. This instance is illustrated by the following set of equilibria in which the reaction is shifted to the extreme left due to the insolubility of the free amine. Usually, however, the concentration of amine produced by hydrolysis is less than that which corresponds to its solubility in water, and therefore the amine is soluble in dilute acid.

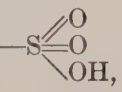
$$\underset{\text{(Solid)}}{R \cdot NH_2} \rightleftharpoons \underset{\text{(Dissolved)}}{R \cdot NH_2} \underset{-H_2O}{\overset{+H_2O}{\rightleftharpoons}} R \cdot NH_3 \cdot OH \underset{-HCl}{\overset{+HCl}{\rightleftharpoons}} \underset{\text{(Dissolved)}}{R \cdot NH_3 \cdot Cl}$$

ACIDIC GROUPS

Among the common acidic groups may be listed the following:

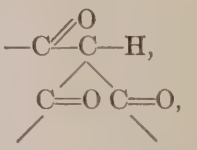
Carboxyl,

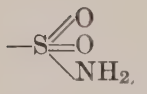
Oxime, 

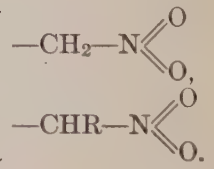
Sulfonic, 

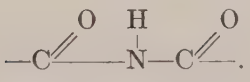
Thiophenol,

Phenol,

Enolic type, 

Sulfone amide, 

I or II nitro 

Imide,  .

Compounds possessing these groups will in general dissolve in dilute NaOH solution since their sodium salts are soluble. The most common exception is to be found among those types which are very feebly acidic. When such members are also high in molecular weight, and therefore very sparingly soluble in water, we may observe insolubility in dilute aqueous alkali.

Problem 3.—The sodium salt of a high molecular weight phenol was prepared by adding the calculated quantity of sodium ethylate to an alcoholic solution of the phenol. The sodium salt was filtered with suction and washed with water. When the compound was analyzed, sodium was found practically absent. Write the equation (showing equilibria) to explain the reactions that took place when the salt was washed with water.

Problem 4.—Write the enolic or "aci" formulas corresponding to the formulas given above for imides, I and II nitro compounds, sulfone amides, and enols. Note that all of the acidic groups may be considered as possessing an hydroxyl group united to an unsaturated atom.

The Solubility Table.—In order to use solubility data effectively in an elementary analytical procedure, it is found convenient to group organic compounds into seven solubility groups. Table XI illustrates such a division. It will be noticed that only a limited number of solvents is used in this solubility plan; viz., water, ether, benzene, cold concentrated H_2SO_4, dilute HCl, and dilute NaOH. The use of a greater number of solvents would lead to a more cumbersome scheme with greater numbers of irregularities; we may, however, secure valuable additional information about any individual group from the use of special solvents.

We shall now proceed to develop this solubility scheme and to place various common classes of compounds into the proper solubility groups. This is done not only to develop an ability to predict solubility behavior, but in order to emphasize the fact that this solubility table, which will be used later in the procedure for analysis, need not be an object of memory work. This table need not be overburdened with many classes of compounds of the " mixed type " where several unlike substituents are present; these types will call forth no special difficulties in the analytical procedure.

To predict solubility we begin with a knowledge of the solubility behavior of hydrocarbons; the solubility of other classes of compounds will then be predicted according to the rules that have been discussed for both " Inert " and " Reaction " solvents. In the laboratory, methane, ethylene, and acetylene, were prepared and collected over water; long before taking up the study of chemistry we knew that gasolene and kerosene (mixtures of hydrocarbons) do not dissolve appreciably in water. In the laboratory, benzene was used for extractions from aqueous solutions partly because of its limited solubility in water. It is apparent, therefore, that *the hydrocarbons* (saturated paraffins, cycloparaffins, unsaturated aliphatics, olefines, and aromatics) *are insoluble in water.*[1] This is true also of the halogen substitution products of the hydrocarbons. Since these compounds contain neither acidic nor basic groups they are classified as indifferents,

[1] The hydrocarbons are insoluble for the purposes of this classification. Hexane is soluble in water only to the extent of 1 part in 1000 and the members higher in this homologous series decrease in solubility approximately according to the rule $1 : \frac{1}{3} : \frac{1}{9} : \frac{1}{27}$. Compare this regularity with the solubilities of *n*-amyl, *n*-hexyl and *n*-octyl alcohols given in Table XII.

and since with few exceptions (pages 19 and 37), they are insoluble in cold concentrated H_2SO_4, we may conclude that the paraffin hydrocarbons, the aromatic hydrocarbons, and their *stable* halogen substitution products fall in Group VI.

TABLE XI

SOLUBILITY TABLE (GENERAL PLAN) *

A Water Soluble		B Water Insoluble				
Group I Soluble in Ether	Group II Insoluble in Ether and Benzene	Group III Soluble in dil. HCl	Group IV Soluble in dil. KOH	Indifferents		
				Hydrocarbons and their oxygen and halogen derivatives		Other indifferents containing, N, S, etc.
				Group V Soluble in cold con. H_2SO_4	Group VI Insoluble in cold con. H_2SO_4	Group VII

The most common oxygen substitution products of the hydrocarbons to be considered are the alcohols, aldehydes, ketones, acids, and esters. The solubility behavior of these derivatives may be predicted by applying Rules I and II. Solubility data for the mono-hydroxy alcohols in water is shown in Table XII.

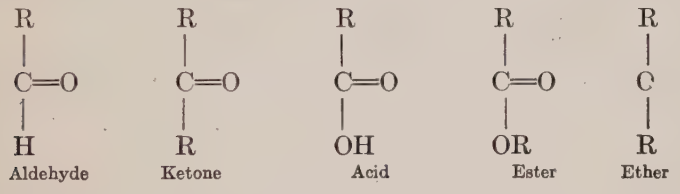
TABLE XII

Alcohol	Solubility in 100 grams H_2O at 20°	Alcohol	Solubility in 100 grams H_2O at 20°
Methyl	∞	Isoamyl	2.5
Ethyl	∞	*n*-Amyl	1.5
Propyl	∞	*n*-Hexyl	0.5
Isopropyl	∞	*n*-Heptyl	0.12
Isobutyl	10	*n*-Octyl	0.03
n-Butyl	9	*sec*-Octyl	0.07

* This Solubility Table is presented in detail form in the chart following page 240.

The lower members in this group of alcohols are closely related to the solvent (water), i.e., the hydroxyl group forms a large proportion of the weight of the molecule; the lower members in the above series are therefore predicted to be very soluble in water and facts agree with this prediction since the first few members are found to be soluble in water in all proportions. However, as we go higher in this homologous series, the compounds become more and more in their solubility behavior like the hydrocarbons from which they are derived (Rule II). The hydrocarbons are however, insoluble in water and this is found to be true of alcohols. of high molecular weight. For practical purposes, C_5 will be considered as the dividing line; mono-hydroxy alcohols with fewer than five carbon atoms will be classified as water-soluble and those with five or more carbons will be grouped as water-insoluble, From analogy in structure to ether, we may predict that the alcohols are soluble in ether. The alcohols of low molecular weight (C_1 to C_5) are placed, therefore, in Group I and those of high molecular weight (indifferents and soluble in H_2SO_4) are placed in Group V.

Similar considerations hold for aldehydes. ketones, acids, and esters.



In the lower members, oxygen forms a considerable proportion of the weight of the molecule and the lower members (less than five carbon atoms) are quite soluble in water.[1] The higher members, again, are found to approach the corresponding hydrocarbons in their solubility behavior; they are insoluble in water (Rule II) but are soluble in ether (Rule I).

Aldehydes, ketones, monocarboxylic acids, and esters of low molecular weight (up to C_4) are placed in Group I, while aldehydes,

[1] The effect of oxygen in producing water solubility in various aliphatic compounds lies in the order $-C\overset{O}{\overset{\parallel}{}}-OH > C=O > OH > C-O-C$

ketones, and esters of high molecular weight, being indifferent and soluble in sulfuric acid, are placed in Group V. The water-insoluble acids are placed, however, in Group IV. Why?

TABLE XIII

SOLUBILITY OF VARIOUS COMPOUNDS IN WATER AT ABOUT 20°–25° IN PARTS PER 100

Number of Carbon Atoms	Aldehyde	Ketone	Acid	Ester
C_1	Miscible	.....	Miscible	
C_2	Miscible	.....	Miscible	Miscible
C_3	20	Miscible	Miscible	
C_4	Iso 11	25	Iso 20	8
	Normal 3.6		Normal ∞	
C_5	1	4.0	4	2

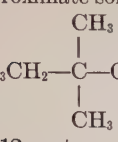
Diethyl ether is soluble in fifteen parts of water at 20°, but the ethers of higher molecular weight are less soluble (Rule II), and therefore fall in Group V.

The mono-amino derivatives of the hydrocarbons are derivatives of a compound (ammonia) which is very soluble in water. The lower members in which the amino group represents a large part of the molecule, are expected therefore to be water-soluble. The higher members will resemble, however, the hydrocarbons (Rule II); they are found to be insoluble in water. The amines of low molecular weight (C_1 to C_6) must be classed in Group I, and those of high molecular weight in Group III because of the presence of the basic group. Among the aralkyl amines,

$$Ar \cdot C_nH_{2n} \cdot NH_2,$$

the benzene nucleus is equivalent in its solubility effect to about four aliphatic carbons. Benzyl amine although possessing seven carbon atoms is water-soluble. Among the branched chain compounds, two methyl side-chains are qualitatively equivalent in solubility effect to one chain-carbon atom.

Problem 5.—Refer to the solubility data in Table XII and predict the approximate solubility in water of (*a*) benzyl alcohol and (*b*) amylene hydrate,



$CH_3CH_2—C(CH_3)_2—OH$. The observed values are (*a*) 3 to 4 parts per 100 and (*b*) 12 parts per 100.

Problem 6.—Aniline, which possesses one CH_2 group less than benzyl amine, is soluble in water only to the extent of 1 part in 30. Explain this apparent anomaly. See also Tables IX and X.

In the discussion of the effect of substituents upon the basicity of amines (page 20), we found that certain groups (acyl groups, a second aryl group, etc.) removed the basicity. Such compounds are often spoken of as " negatively substituted amines," and must be classified among the indifferents, and since they contain nitrogen are placed in Group VII, irrespective of their behavior toward sulfuric acid. Amides of low molecular weight ($R \cdot CO \cdot NH_2$, where R is $C_{1\text{ to }4}$) are water-soluble and sparingly soluble in the hydrocarbon solvents; they therefore fall mainly in Group II.

It is to be noted that although solubility in ether or benzene is used to differentiate between Groups I and II, these solvents are not required for assigning any classes of compounds to the remaining five groups of the Table. Thus, certain compounds falling into Groups III or IV may be very soluble in ether, while other members are almost insoluble in ether. Similar variations are noticed especially in Group VII. These are facts of value to an experienced analyst but they do not affect the classification into the seven main groups; for further subdivision of these groups such solubility data might be utilized.

The Effect of Polysubstitution in the Oxygenated Derivatives of the Hydrocarbons.—The mono-hydroxy and mono-carboxy derivatives of the hydrocarbons are soluble in ether and in benzene. The presence of several hydroxyl or of several carboxyl groups will decrease solubility not only in benzene but also in ether. The compounds become more like water in structure and less like the hydrocarbons and ether.

For example, propyl alcohol is miscible with ether and benzene in all proportions, but the presence of two or three hydroxyl groups causes a very low solubility in ether and insolubility in benzene. Such compounds will be placed in Group II. As we

TABLE XIV

Alcohols.	Solubility in ether.	Solubility in benzene
$CH_3CH_2CH_2OH$.....	Miscible	Miscible
$CH_3CHOH \cdot CH_2OH$.....	Slightly soluble (7%)	Almost insoluble
$CH_2OH \cdot CH_2 \cdot CH_2OH$.....	Slightly soluble (3%)	Insoluble
$CH_2OH \cdot CHOH \cdot CH_2OH$.....	Insoluble	Insoluble

go higher in a given homologous series Rule II must be applied. For example, the compound

$$CH_3CH_2CH_2CH_2CH_2CH_2 \cdot CHOH \cdot CH_2OH$$

will be appreciably soluble in ether, despite the presence of two hydroxyl groups.

The dicarboxylic acids are solid compounds the solubility behavior of which has received consideration in the discussion of Rule IV.

The simple carbohydrates are rich in hydroxyl groups and are consequently very soluble in water but insoluble in ether. High molecular weight carbohydrates $(C_6H_{10}O_5)_x$, such as starches and cellulose, are insoluble in water as well as in ether. The insolubility of most starches in cold water is controlled also by the physical structure of the starch granules. In hot water, the external membranes of the cells are broken and a colloidal starch solution results.

The presence of both hydroxyl and carboxyl groups in the same molecule, especially in low molecular weight compounds, tends to cause ether insolubility. In the absence of any unusual complexity in the solid state, there results great solubility in water; examples are glycolic, lactic, tartaric, malic, and citric acids, which therefore fall in Group II. This discussion applies also to low molecular weight amino acids where we note the additional effect of salt formation. Salts not only of this type but of organic acidic substances with inorganic bases and of organic bases with mineral acids, with only a limited number of exceptions, are insoluble in ether.

Space will not permit the discussion of additional solubility data, but, in order to emphasize further the fact that the Solubility Table need not be treated as a piece of memory work, an additional class exercise is assigned at the end of Chapter VIII.

CHAPTER III

CLASSIFICATION REACTIONS OF ORGANIC COMPOUNDS

HYDROCARBONS AND THEIR OXYGEN AND HALOGEN DERIVATIVES

THE study of the elements of organic chemistry will have made familiar the characteristic reactions of the common classes of organic compounds, viz., the reactions of the carboxyl group, the carbonyl group, the hydroxyl group, the nitro group, the amine group, the aryl hydrocarbon group, etc. The following discussion, together with the experimental work in Chapter IX, will consist of a partial review of the facts that are furnished so plentifully in a general course in organic chemistry. This review will offer an opportunity for a reclassification of the information which is unfortunately too often first studied in a memorizing fashion. A systematic review from a different standpoint and a regrouping of this information for the purposes of qualitative analysis is of value as a general training for the chemist.

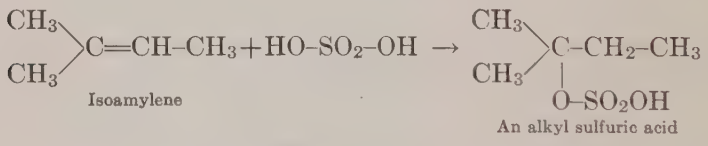
Qualitative organic analysis is possible because of the facts of homology; all the members in a given homologous series exhibit the same *kind* of chemical reactions, but they differ in the *velocity* of reaction. Another important problem for consideration is the effect of a given atom or group of atoms in modifying the homologous tests of other groups simultaneously present in the molecule. It is one of the functions of qualitative analysis to teach some of this detailed information, particularly in connection with the actual laboratory study.

Most of the reactions to be discussed are adaptable to the differentiation between various classes of possibilities within a given solubility group; others possess value mainly in testing for a limited number of individual compounds; a third type is adapted mainly to quantitative work after a search has been limited to a

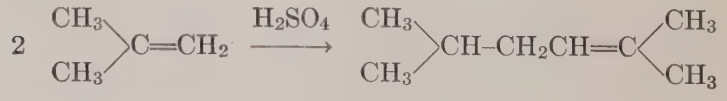
certain class; and a fourth type is useful after the identification has been narrowed down to only a few individuals within a given class when standardized reactions are required for the preparation of derivatives.

Not only is a familiarity with the reactions of organic chemistry required for the purposes of qualitative organic analysis, but it is important also to know the conditions under which reactions are applied and the limitations and interferences to which a test may be subject under any set of given experimental conditions. Such a knowledge must come primarily from the laboratory.

Behavior of Hydrocarbons Toward Cold Concentrated Sulfuric Acid.—With the exception of the unsaturated members, the hydrocarbons and their halogen derivatives will be found in Solubility Group VI. Compounds of the olefine type will be placed in Group V, although they do not dissolve in cold concentrated sulfuric acid readily, as is the case with oxygen derivatives of the hydrocarbons. Compounds of the ethylene series react with sulfuric acid in the following manner, the unsaturated carbon atoms showing a preference for the acid radical in the following order: Tertiary > secondary > primary.



The above reaction proceeds smoothly under suitable experimental conditions, viz., proper temperature control and acid concentration. The solution of alkyl sulfuric acid may be poured into water, neutralized with excess alkali, and the corresponding alcohol recovered by distillation. When an olefine is treated with concentrated sulfuric acid without special precautions, as in the usual solubility test, only a portion of the compound is converted into a soluble alkyl sulfuric acid, the remaining portion being polymerized to compounds of limited solubility in sulfuric acid. The first step in such a polymerization may be represented thus:



The mother substance, ethylene, is fairly resistant to polymerization but its homologs, beginning with propylene, are more reactive. Amylene may be converted with 85 per cent sulfuric acid at 0° into an almost quantitative yield of the corresponding alkyl sulfuric acid but with less precaution it yields polymers containing ten, fifteen, and twenty carbon atoms.

Problem 7.—When *n*-butyl alcohol is catalytically dehydrated it is converted mainly into a mixture of *n*-butene-1 and 2-methylpropene-1. Write the equations to represent the reactions which take place when this gas mixture is absorbed in sulfuric acid under conditions that do not lead to polymerization.

Although paraffin hydrocarbons do not dissolve in sulfuric acid, technical products such as petroleum ether, ligroin, gasolene, kerosene, etc., which are often represented in text-books as typical mixtures of paraffin hydrocarbons, exhibit considerable reaction with sulfuric acid, due mainly to the presence of unsaturated compounds. The amount of unsaturation in these technical products has increased greatly during recent years, with the advent of " cracking processes " for the production of lower-boiling fractions from petroleum.

Aromatic hydrocarbons are insoluble in cold concentrated sulfuric acid under the conditions chosen for the solubility tests. A few individual members among the poly-methyl benzenes are sulfonated *slowly* by cold concentrated sulfuric acid but the reaction is not liable to be confused with the usual nonsulfonating solubility test.

The Unsaturated Hydrocarbons.—Unsaturation in organic compounds may be detected by a variety of addition reactions. The addition of sulfuric acid to an ethylene double union has already been illustrated. Other reagents which may be added are halogens, halogen acids, ammonia and substituted ammonias, diazomethane, ozone, hypohalites, nitrosylchloride, hydrogen peroxide (H_2O+O), tautomeric esters, organo-metallic compounds, hydrogen, etc. Some of these addition reactions are of great technical importance; others are of value in synthetical work, particularly in connection with the determination of structure of compounds.

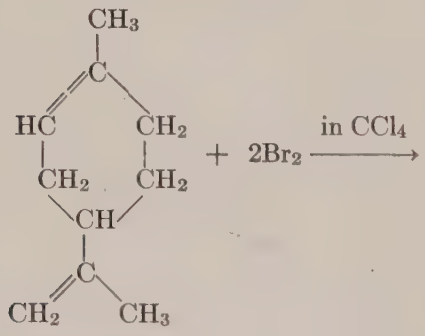
Only two of the above addition reactions are convenient and general enough for use in elementary qualitative work. These two reactions are:

(*a*) Addition of halogen, usually of bromine, and

(*b*) Oxidation at the position of unsaturation by $KMnO_4$ solution.

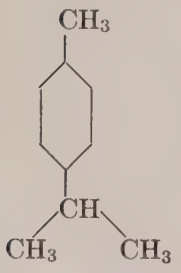
These reactions are typical not merely of unsaturated hydrocarbons but of unsaturated linkages in general. In the presence of certain negative groups, addition of bromine may be very slow but in such cases the permanganate test will be found sufficiently sensitive. Bromine may be decolorized, due to substitution reactions, particularly among the phenols, aromatic amines, enols, certain aldehydes, etc., but in such instances halogen acid may be detected as a by-product. The above-mentioned types will also respond to the permanganate test: these considerations are again studied in connection with the actual experimental work of Chapter IX. What inorganic compounds might be responsible for decolorization of bromine and permanganate?

By means of bromine addition, we may differentiate the unsaturated hydrocarbons from the saturated types.



Terpene (dipentene)

Tetrabromo addition product of dipentene



p-Methyl isopropyl benzene (cymene)

$+ Br_2 \xrightarrow{\text{in } CCl_4}$ No reaction under same conditions.

Problem 8.—Write the formulas for the products obtained from (*a*) the addition of HBr to dipentene, (*b*) the addition of ozone to isoprene, (*c*) the action of bromine water upon ethylene. J. Chem. Soc., **111**, 242 (1917).

Bromine addition thus serves to differentiate between two main groups of hydrocarbons; the reaction is adaptable also to quantitative determinations (page 170) and as such is used extensively in quantitative analysis of certain classes of organic compounds. Only a few relatively unimportant hydrocarbons fail to respond to this test. On the other hand, among the unsaturated derivatives of hydrocarbons, there is considerable variation in the ease of reaction with bromine.

TABLE XV

DIFFERENTIATION BETWEEN HYDROCARBONS

Hydrocarbons+5 per cent Br_2 in CCl_4 at 0° to 20°

A		B	
Molecular* quantities of Br_2 decolorized without production of a considerable quantity of HBr.		No addition of Br_2 in the cold and in diffused light.	
Unsaturated hydrocarbons		Hydrocarbons of saturated type	
1	2	1	2
Ethylene type	Acetylene type	Paraffins, insoluble in dimethyl sulfate. Not sulfonated by $H_2SO_4 \cdot SO_3$	Aromatics, soluble in dimethyl sulfate. Sulfonated by $H_2SO_4 \cdot SO_3$

* From the boiling-point of an unknown of a given type, the approximate number of carbon atoms in the molecule may be predicted.

A differentiation between the two subclasses A_1 and A_2 is seldom necessary since this is accomplished in connection with the final identification of the individual compounds. A triple union will usually add four atoms of bromine, but this is true also of the diolefines. When both hydrogens of acetylene are replaced by so-called negative groups (phenyl, carboxyl, etc.) only two atoms of bromine are added. Ethylene derivatives containing such negative groups add bromine rather slowly. (Example: Addition of Br_2 to cinnamic acid.)

Oxidation with Potassium Permanganate.—The first effect of permanganate upon an ethylene union probably consists in the

formation of an oxide which usually is detected only in the form of its hydrolytic product.

$$R\text{–}CH{=}CH_2 \xrightarrow{O} \left[R\text{–}CH\text{—}CH_2 \right] \xrightarrow{H_2O} R\text{–}CHOH\text{–}CH_2OH$$

The resulting glycol, as such, would be comparatively stable towards permanganate oxidation but, while in the process of formation, it is readily oxidized past this stage to yield the corresponding ketone and aldehyde groups, the final result being a break between the two carbon atoms initially united through the double union. The reaction has proven of great value as a means of structure proof. Write the equations for the subsequent steps in the oxidation of the above glycol.

Acetylene and its derivatives of the type R–C≡C–H form organometallic derivatives with ammoniacal cuprous chloride or with ammoniacal silver nitrate. R–C≡C–Ag and R–C≡C–Cu. These precipitates although explosive when dry, have been used for quantitative determinations. (Ber. **20**, 3081 (1887).) An alcoholic silver nitrate solution precipitates a double salt.

$$R\text{–}C{\equiv}CH + 2AgNO_3 \rightarrow R\text{–}C{\equiv}C\text{–}Ag\cdot AgNO_3 + HNO_3.$$

Titration of the nitric acid liberated furnishes a volumetric method of analysis.[1]

It has already been pointed out that ethylene derivatives may under certain conditions add sulfuric acid to yield alkyl sulfuric acids from which the corresponding alcohol may be recovered. The analogous reaction may be applied to triple-bonded compounds, but the final product will be not an alcohol but an aldehyde or ketone. Write equations to illustrate such a reaction.

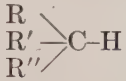
The Saturated Aliphatic Hydrocarbons.—For the differentiation between the saturated aliphatic and aromatic hydrocarbons, the reactions typical of the benzene nucleus are applied. The paraffin hydrocarbons are inert towards many of the reagents to which the members of the aromatic series respond; the most important reaction of the paraffins is substitution by halogens and this reaction is not suitable for qualitative application. The paraffin hydrocarbons usually met are the various fractions from petroleum and in dealing with these products special provision must be made for reaction due to the presence of not inconsiderable quantities of unsaturated products.

[1] Ann. chim. phys. (6) **15**, 429 (1888); Ber. **25**, 2249 (1892).

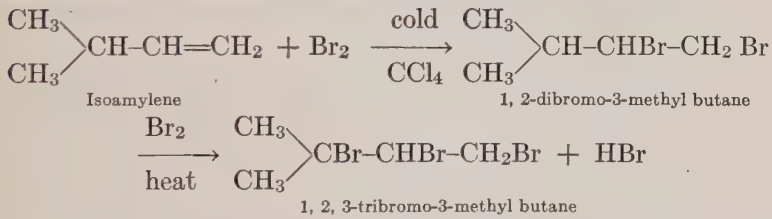
The cyclo-paraffins, with the exception of cyclopropane, which behaves as an unsaturated hydrocarbon toward bromine (but not towards $KMnO_4$), are similar in reactions to the normal paraffins. This class of compounds is becoming of increasing importance because of the development of the catalytic nickel method for the hydrogenation of aromatic hydrocarbons.

Problem 9.—Write the structural equation to illustrate the reaction between cyclopropane and Br_2.

Among the paraffin hydrocarbons, the greatest reactivity is found among members which possess a tertiary carbon atom, viz.:



The hydrogen on the tertiary carbon may be appreciably attacked by nitric acid, fuming sulfuric acid and by oxidizing agents. Substitution by halogens also takes place more readily. It is necessary for this reason that the bromine titration of unsaturated compounds be carried out at a low temperature and in the presence of a diluent like carbon tetrachloride. For example, amylene, which possesses a tertiary carbon, adds bromine almost quantitatively under the specified conditions. At a higher temperature, the tertiary hydrogen may become involved in the reaction.



Reactions of Aromatic Hydrocarbons.—The typical reactions of aromatic hydrocarbons are:

1. Direct sulfonation,
2. Direct nitration,
3. Oxidation of side chains,
4. Controllable halogenation,
5. Reactivity in the Friedel and Crafts Reaction.

These reactions are typical also of many derivatives of aromatic hydrocarbons; in fact, the presence of certain substituents, like the amine and phenolic groups, may facilitate substitution into the benzene nucleus; on the other hand, certain other substituents, like the nitro and sulfonic acid groups, will cause sub-

stitution to take place with more difficulty. Nevertheless, among substitution products of aromatic hydrocarbons, these reactions are relatively unimportant from the standpoint of classification, but they are especially valuable for the preparation of derivatives.

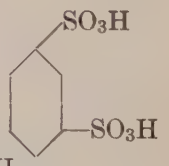
Application of direct sulfonation is the most convenient reaction for the differentiation of aromatic hydrocarbons from the saturated aliphatic type. The various aromatic hydrocarbons differ considerably in the ease of reaction with sulfuric acid; some members sulfonate *slowly* with concentrated (95 per cent) sulfuric acid without heating, others require concentrated acid with heating, while still others require fuming sulfuric acid occasionally with heating. The most convenient reagent for the differentiation is fuming sulfuric acid containing 20 per cent of the anhydride. *The sign of reaction is the generation of heat and the gradual but complete solution of the hydrocarbon without excessive charring.* Impure paraffin hydrocarbons may show considerable charring due to the presence of unsaturated compounds, but the main portion of the product is not attacked.

Benzene reacts extremely slowly even with hot concentrated H_2SO_4. In fuming sulfuric acid ($H_2SO_4 \cdot SO_3$), it dissolves readily and completely, considerable heat being liberated. The second sulfonic acid group enters less readily and the third group only with great difficulty.

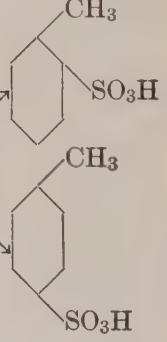
$$C_6H_6 + H_2SO_4 \xrightarrow{SO_3} C_6H_5\text{–}S(=O)_2\text{–}OH + H_2O$$

Benzene sulfonic acid

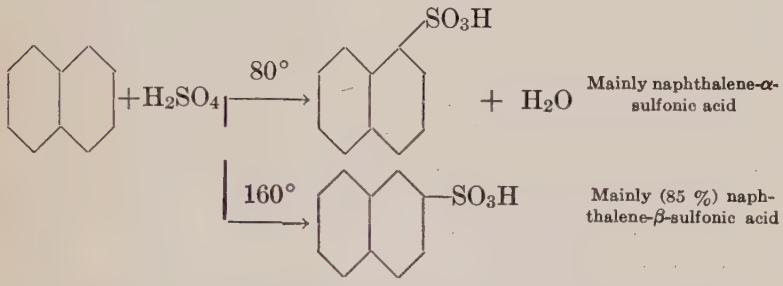
$$\xrightarrow[\text{heat}]{H_2SO_4 \cdot SO_3}$$



$$C_6H_5\text{–}CH_3 + HO\text{–}SO_2\text{–}OH \longrightarrow$$



Toluene sulfonates more readily than benzene, while *o*- and *m*-xylene and mesitylene may be slowly sulfonated with 95 per cent H_2SO_4, even without heating. Para derivatives, such as *p*-xylene, dissolve less readily (separation of the xylenes), while *p*-dihalogen benzenes require 20 per cent fuming sulfuric acid and heating to 100° to 120° for sulfonation. Substitution in naphthalene takes place more readily than in benzene and therefore concentrated H_2SO_4 may be used.



Problem 10.—In the sulfonation of benzene with $H_2SO_4 \cdot SO_3$, a trace of diphenyl sulfone is formed. Write the equation for the reaction. Separate a mixture of *o*- and *p*-chlorotoluene by means of sulfonation reactions.

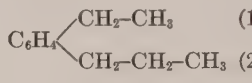
Although sulfonation is an important "classification reaction," it is of less importance as a "characterizing reaction." To be sure, the sulfonic acids may be isolated as the sodium salts, the latter converted (after drying) into the acyl chlorides and characterized either as such or in the form of the amides. More direct characterization methods are usually available. A few sulfonic acids may be isolated as such, but in general they are difficult to isolate because of their extreme solubility in water.

Direct nitration, either with fuming HNO_3 or with a nitrating mixture containing equal volumes of concentrated HNO_3 (1.4 sp. gr.) and concentrated H_2SO_4, is sometimes used for the differentiation between saturated aliphatic and aromatic hydrocarbons. Its disadvantage consists in the fact that the resultant nitration product often possesses a solubility behavior similar to that of the original unknown. Nitration is of greater value as a reaction for the preparation of derivatives.

Oxidation of side-chains, with the resultant formation of carboxyl groups, is another typical reaction of aromatic hydrocarbons and of many of their derivatives. This reaction is of minor importance for the purposes of classification but again it is of great value in the preparation of derivatives. It will therefore be discussed in Chapter X.

Problem 11.—Review the rules governing the positions taken by substituting groups introduced into the benzene nucleus. Place the groups NO_2, OH, Cl, Br, NH_2, $NH \cdot COCH_3$, SO_3H, CH_3, OC_2H_5 and CO_2H approximately in the order of their directing ability. Cf. Annual Reports **15**, 75 (1918).

Problem 12.—What organic acid is formed when



is oxidized with neutral or alkaline permanganate?

Differentiation between Aromatic and Paraffin Hydrocarbons.—Differentiation between these two classes of hydrocarbons by means of the sulfonation test has already been discussed above. To some extent, sulfonation may be applied also when we are dealing with halogen derivatives of hydrocarbons, although usually considerable decomposition takes place with the evolution of halogen acid in the case of the chlorides and bromides and of free iodine in the case of iodides. Halogen attached directly to the benzene nucleus is stable toward sulfonation.

A more convenient method for differentiation between the aromatic and paraffin hydrocarbons is the dimethyl sulfate solubility test (page 135). The paraffin hydrocarbons do not dissolve appreciably in this reagent, whereas aromatic hydrocarbons in general dissolve in all proportions, due probably to the formation of an addition product between the ester and the aromatic nucleus. The aromatic hydrocarbons may be recovered from dimethyl sulfate by saponifying the latter with dilute alkali. *This method of differentiation does not extend to the halogen derivatives of these hydrocarbons.*

The use of dimethyl sulfate[1] is illustrated in the laboratory work. Special precautions must be taken in the use of this reagent since it is reported to be extremely toxic.

The Reactivities of Organic Halogen Compounds.—Halogen compounds of a given type but differing in the nature of the halogen, possess the following order of reactivity toward the usual organic laboratory reagents: I > Br > Cl. Among the halogen substitution products of paraffin hydrocarbons, the reactivity for a given halogen united to tertiary, secondary, or primary carbon atoms respectively, is in the order mentioned, the tertiary halogen compound possessing the greatest mobility. Halogen compounds in which the halogen (X) is united directly to an unsaturated carbon atom of the type C=C, possess increased

[1] Chem. Ind. **23**, 559 (1900).

stability. Unsaturation on the β-carbon gives increased activity. Substitution by oxygen on the α-carbon increases the activity.

$CH_3–CH{=}CHX$ is more stable than $CH_3–CH_2CH_2X$ or $CH_2{=}CH–CH_2X$.

$C_6H_4\begin{cases}CH_3\\X\end{cases}$ is more stable than $C_6H_5CH_2X$.

$\left.\begin{matrix}R–C(=O)–X\\R–O–CH_2X\end{matrix}\right\}$ are very reactive.

Carboxylic acids that are aliphatic in nature and which possess a halogen on the gamma carbon exhibit greater reactivity toward elimination of HX (lactone formation) than do the α and β substituted acids.

$$CH_3–\underset{Br}{\overset{H}{C}}–CH_2CH_2C(=O)–OH \xrightarrow{Na_2CO_3\ sol'n} CH_3–\underset{\llcorner O \text{———} \lrcorner}{\overset{H}{C}}–CH_2–CH_2–C{=}O$$

Lactone or inner ester

The usual tests employed for determining the relative reactivities of halogen compounds are:

(*a*) Reactivity towards tertiary amines,
(*b*) Reactivity towards alcoholic KOH,
(*c*) Reactivity towards alcoholic $AgNO_3$.

The reactions of organic halogen compounds with tertiary amines, resulting in the formation of quaternary ammonium compounds, has been used extensively for quantitative measurements of reactivity the degree of which is usually expressed in the form of a velocity constant. Since the ammonium derivative formed in the reaction possesses ionizable halogen, the amount of reaction up to any given time may be determined conveniently by volumetric methods.

Methods (*b*) and (*c*) are used more often in connection with qualitative work in the laboratory. A small amount (about 0.2 g.)

of the organic compound is dissolved in a few cc. of a 5 per cent solution of KOH in aldehyde-free ethyl alcohol. The mixture is boiled gently for about a minute and is then diluted with several volumes of water and acidified with HNO_3. Any organic compound separating upon dilution must be removed by filtration. Ionizable halogen in the aqueous solution is then tested for by means of the usual aqueous $AgNO_3$ reagent.

The alcoholic $AgNO_3$ test is assigned in Chapter IX in connection with the laboratory work. It may be applied more rapidly than the alcoholic potash test and is almost as satisfactory. A saturated solution of $AgNO_3$ in absolute alcohol is used as a reagent, the alcohol serving as a common solvent for both the $AgNO_3$ and the organic compound to be tested. The test is not applicable to unsaturated compounds, some of which may form insoluble addition products with $AgNO_3$ in alcoholic solution; neither should it be applied to compounds of the salt type. Certain acidic substances may produce a precipitate of an insoluble silver salt which might be mistaken for silver halide. Care must be taken therefore in applying the test to substances of this character. Water-soluble substances containing halogen should be tested with aqueous $AgNO_3$ after acidification with HNO_3. But here also precautions are necessary similar to those taken with the alcoholic solution.

The organic halogen compounds may be placed in four groups from the standpoint of their reactivity towards $AgNO_3$.

(1) Water-soluble compounds containing ionizable halogen, or compounds such as acid halides of low molecular weight, which react readily with water to form ionizable halogen compounds, will react instantaneously, even with aqueous $AgNO_3$.
(2) Water-insoluble acyl halides, tertiary halogen compounds, etc., react instantaneously with alcoholic $AgNO_3$.
(3) Primary and secondary halogen compounds in the aliphatic series or aromatic compounds containing halogen in the side-chain, react slowly with alcoholic $AgNO_3$ but fairly rapidly on heating. Some chlorine derivatives are exceptions to this rule.
(4) Aromatic halogen compounds containing halogen in the ring do not react even upon heating. Compounds of this type substituted by a nitro group in the ortho position, however, possess considerable activity.

The Friedel and Crafts Reaction is a method of introducing a side-chain into the benzene nucleus by treating an aromatic hydrocarbon with a reactive

halogen compound in the presence of anhydrous aluminum chloride. The reaction is sometimes applied in order to differentiate between certain classes of halogen compounds. It is occasionally also used to differentiate between paraffin and aromatic hydrocarbons. The main objection to the test is that an appreciable quantity of pure material is required.

Problem 13.—Explain exactly how the Friedel and Crafts Reaction may be applied in the laboratory in order to (*a*) differentiate cyclohexane from benzene, and (*b*) benzyl chloride from *o*-chlorotoluene.

The Acyl Chlorides.—These compounds are chiefly of value as reagents for the testing of amines, alcohols, and phenols. When an unknown containing a very reactive halogen atom is suspected of being an acyl halide, the usual experimental conditions are reversed and a known amine is used as a reagent for the unknown.

Problem 14.—Write the reaction which takes place between *p*-toluene sulfonyl chloride and aqueous NH_3. What is formed when the reaction product is treated with a slightly alkaline solution containing one mole of NaOCl?

The Indifferent Oxygen Derivatives of Hydrocarbons: Aldehydes, Ketones, Esters, Anhydrides, Alcohols, and Ethers.—With the exception of a relatively small number of members of low molecular weight (Group I), these compounds fall into Solubility Group V. Contrary to the usual assumption, relatively few members from the above series are decomposed by cold concentrated sulfuric acid. Solubility in sulfuric acid without decomposition is by no means peculiar to the ethers. Differentiation between Groups V and VI, however, is not limited to solubility without decomposition; in fact, we have already discussed the behavior of the unsaturated hydrocarbons in this respect. Solubility with discoloration and partial polymerization will be noted especially with aliphatic aldehydes; ethers of the acetal type will readily hydrolyze; and marked decomposition will be noted with benzyl alcohol and its derivatives, a decomposition which may possibly be typical of many aromatic compounds with the $-CH_2OH$ side-chain. The complete decomposition of a product of the latter type with the production of solid products insoluble in concentrated H_2SO_4 must be accepted as evidence that the unknown is not a hydrocarbon.

In testing for the compounds in Group V, the following order is preferable:

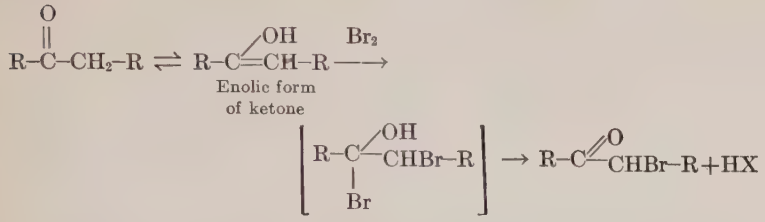
TABLE XVI

SOLUBILITY GROUP V, ALDEHYDES, KETONES, ESTERS (ANHYDRIDES), ALCOHOLS, ETHERS, ETC. APPLY THE PHENYLHYDRAZINE TEST

Positive reaction. Aldehyde or ketone. Apply tests to differentiate	Negative test. Esters (anhydrides), alcohols, ethers, unsaturated HC. Apply saponification test		
(Anhydrides will interfere. See page 45.)	Positive reaction. Esters and anhydrides	Negative reaction. Alcohols, ethers, unsaturated HC. Apply acyl halide test	
		Positive reaction. Alcohols	Negative reaction. Ethers and unsaturated HC

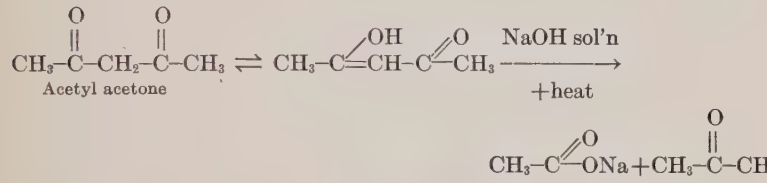
Both aldehydes and ketones possess the carbonyl group $-C\overset{O}{\overset{\|}{\leftarrow}}$ and their most important reactions are therefore the typical reactions of this group. The speed of reaction of the carbonyl group, and, to some extent also the kind of reaction, is dependent upon the groups united to the carbonyl. In aldehydes, $R-C\overset{O}{\overset{\|}{\leftarrow}}H$, the carbonyl group is united to a hydrogen atom, whereas in ketones $R-C\overset{O}{\overset{\|}{\leftarrow}}R'$, the aldehyde hydrogen is replaced by a radical of higher molecular weight. In additive reactions, the aldehydes will therefore show a greater reaction velocity; individual ketones will exhibit decreased reaction velocity with increase in molecular weight of the radical R^1. Differentiation between aldehydes and ketones may be based upon this difference in the ease of reaction. Since the hydrogen of the $-C\overset{O}{\overset{\|}{\leftarrow}}H$ is readily oxidized to hydroxyl, another differentiation between aldehydes and ketones is found in differences in the ease of oxidation.

The carbonyl group increases the mobility of the hydrogens on adjacent carbon atoms. For this reason, substitution by halogens takes place more readily with these classes of compounds than with the hydrocarbons.



A methylene (CH_2) group adjacent to the carbonyl group is often spoken of as a reactive methylene. It takes part more readily in condensation, oxidation, halogenation and other reactions than does the normal methylene group in hydrocarbons.

A methylene group adjacent to two carbonyl groups exhibits unusual reactivity, due to an increase in the amount of enolization. Such compounds form sodium salts with alcoholic sodium ethylate and are of considerable importance in synthetical work. Some of these enols may behave toward alkali treatment in a manner suggestive of the saponification of esters.



Although the various reactions just discussed are seldom used for classification purposes in elementary analytical work, they are of importance in connection with possible interference with the usual tests.

Problem 15.—Write the reactions for (*a*) the ketone splitting of acetoacetic ester, and (*b*) the acid splitting of the same ester.

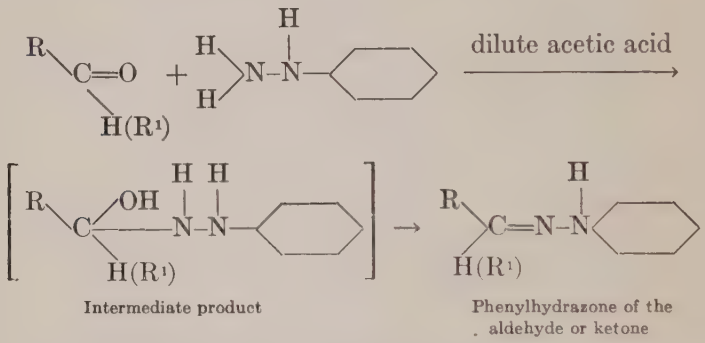
Problem 16.—Upon saponifying an ester with concentrated alkali, an alcohol and an acid are obtained. Which classes of aldehydes also yield acids and alcohols under similar treatment? Write the equations.

Other common classes of compounds which, according to the linking theory, possess carbonyl groups, are carboxylic acids, esters, amides, acyl halides, etc. These groups, however, do not exhibit the typical carbonyl condensation reactions.

General Test for Aldehydes and Ketones.—Phenylhydrazine reacts with both aldehydes and ketones to yield phenylhydrazones. The reaction is catalyzed by the presence of a weak acid like acetic, but strong acids may prevent the reaction; for example, phenylhydrazine hydrochloride may not react unless an equivalent amount of sodium acetate is added. The sign of

reaction is the formation of a sparingly soluble phenylhydrazone, which is insufficiently basic to dissolve in dilute acid.

When a clear solution of phenylhydrazine in dilute acetic acid is added to a dilute aqueous solution of an aldehyde or ketone of low molecular weight, an immediate and almost quantitative precipitation of the corresponding phenylhydrazone is noted. For water insoluble carbonyl compounds, a modified procedure is proposed (Chapter IX). When the phenylhydrazone of an unknown is found to be a solid, it may be recrystallized and used as a derivative.



This reaction has been adapted to quantitative volumetric work[1] as is also the case with certain other condensation reactions, particularly the reaction with hydroxylamine.[2]

In addition to the condensation with phenylhydrazine, the aldehydes and ketones undergo analogous reactions with other substituted ammonias. This topic will be discussed further in connection with the preparation of derivatives, in Chapter X.

Discussion of the Phenylhydrazine Reaction.—The dilute acetic acid solution of phenyldrazine should be prepared just before using. After it has been allowed to stand even at room temperature for several days, an appreciable amount of the sparingly soluble acetyl derivatives of phenylhydrazine will have formed. In general, the phenylhydrazones are much less soluble in various solvents than are the corresponding aldehydes and ketones. A convenient method of applying the test to water insoluble compounds therefore consists in dissolving the carbonyl compound in a small amount of alcohol and adding water drop by drop until the solution is exactly at the saturation point. An amount of pure liquid phenylhydrazine equal to that of the unknown is then added. In the case of most aldehydes, an

[1] Monatsh. **13**, 299 (1892). [2] Analyst **34**, 14 (1909).

almost immediate precipitation of the phenylhydrazone takes place, due to the fact that it is less soluble in the dilute alcohol than is the aldehyde. If no precipitation takes place within one minute's time, one drop of glacial acetic acid is added in order to catalyze the reaction.

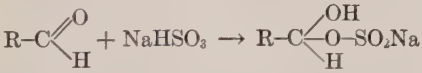
The various ketones differ greatly in their speeds of reaction with phenylhydrazine, some precipitating after a few seconds, others after several minutes, whereas members of very high molecular weight may require a considerably longer time. The rapid reaction of most aldehydes without the addition of a drop of acetic acid to act as a catalytic agent may possibly be explained by the fact that many of the aldehydes contain a trace of acid as an impurity. Aldehydes of special purity show slower reactions, corresponding more closely to the ketone reaction.

A number of salts of phenylhydrazine are only sparingly soluble in water; this is true of the oxalate, sulfate, phosphate, etc. It is therefore important that this be kept in mind when phenylhydrazine is used in testing for the presence of aldehydes or ketones in aqueous solutions which might contain also other substances.

Among the esters, a few members, for example, methyl oxalate, may be sufficiently reactive to combine with the reagent to form an acyl derivative, the precipitation of which might be confused with the test for the carbonyl group. This is true also of the anhydrides.

Phenylhydrazine is important in testing certain sugars (Chapter V).

In addition to the phenylhydrazine test, many other reactions may be adapted, with suitable limitations, as tests for the carbonyl group. In general, these reactions are not as convenient and satisfactory as the test outlined above. The formation of addition products with sodium acid sulfite is not as general as is often suggested in text-books. Aldehydes and low molecular weight ketones react readily but the higher ketones and particularly aromatic ketones show very little reaction, particularly when the ketone group is adjacent to the aromatic nucleus. The reaction is almost as satisfactory for differentiation between aldehydes and ketones as for a general test, and somewhat unsatisfactory for either purpose. The sulfite addition products are sometimes quite soluble in water.



The reaction is often of value in purifying aldehydes and ketones. The organic compound may be recovered by treatment with either dilute acid or alkali (Na_2CO_3). A common source of error in applying the test to an alcoholic solution of an unknown consists in a precipitation of the sodium bisulfite itself, due to its lower solubility in alcohol.

Problem 17.—Write structural equations for the following reactions: (*a*) Benzaldehyde and concentrated alkali in the Cannizzaro reaction, (*b*) formaldehyde+ethyl alcohol in the presence of a small quantity of dry HCl, (*c*) a ketone+aqueous HCN, (*d*) acetone+an aqueous solution of

NH_4Cl and KCN, (*e*) acetaldehyde+NH_3 in dry ether, (*f*) benzaldehyde or furfural+aqueous NH_3, (*g*) benzaldehyde+aniline (alcoholic solution), (*h*) magnesium ethyl bromide and *n*-heptanal.

The Differentiation between Aldehydes and Ketones.—(*a*) *The Ammoniacal Silver Nitrate Test.* Aldehydes are readily oxidized with ammoniacal silver nitrate solution, whereas ketones are more stable.

$$R\text{–}C\begin{matrix}\diagup\!\!\!=O\\ \diagdown H\end{matrix} + Ag_2O\left(\begin{matrix}\text{in sol'n as}\\ Ag(NH_3)_xOH\end{matrix}\right) \rightarrow R\text{–}C\begin{matrix}\diagup\!\!\!=O\\ \diagdown\!\!-O\text{–}NH_4\end{matrix} + 2Ag \downarrow$$

(*b*) *The Fuchsin Aldehyde Test.*—Aldehydes restore color to Fuchsin Aldehyde Reagent whereas ketones do not. The reagent is a dilute solution of rosaniline or fuchsin hydrochloride (magenta) that has been decolorized by sulfur dioxide.

$$\underset{\text{Crimson color.}}{\text{Rosaniline HCl}} + 2H_2SO_3 \rightarrow (H_2N\cdot C_6H_4)_2 : C(SO_3H)\cdot C_6H_4\cdot NH\cdot SO_2H$$

Colorless

The aldehyde reverses this reaction due to a removal of H_2SO_3 from the methane carbon and a regeneration of the quinoid linkage. The restored color is not identical with the original fuchsin color but possesses a distinct bluish tinge. This is due to a reaction between the aldehyde and amino groups. The recently proposed formula for the aldehyde-dye,

$$(R\cdot CHOH\cdot O\cdot SO\cdot NH\cdot C_6H_4)_2 : C : C_6H_4 : NH$$

(Ber. 54, 2534) is still open to question.

In general those reagents which remove sulfurous acid will restore the fuchsin color. This is true of organic amines, inorganic alkalis, and even of certain hydrolysable salts. Heating the reagent restores the color due to the dissociation of the fuchsin-sulfite compound. Although the restored color lacks the typical bluish tinge produced by aldehydes, it is always advisable to apply the test in the cold and to bear in mind the possible interferences.

General Test for Esters and Anhydrides.—When a compound responds to a test for an aldehyde or ketone, other reactive groups may of course be present also. If such should be the case, evidence will be found in connection with the subsequent tests, and particularly in connection with the physical constants of the unknown and its derivatives. Consultation of tables of physical constants before applying class reactions is unjustifiable and liable to cause unnecessary work because it is apt to be misleading. On the other hand, after a typical group has been located, then physical constants will be of value in indicating other possible groups to be tested for (with due consideration for complications caused by the simultaneous presence of several groups).

The general test for esters (including lactones) and anhydrides is saponification with alkali. Ethers will remain unaffected under the experimental conditions chosen, but aldehydes may be decomposed. See Problem 17.

Problem 18.—Write structural equations to illustrate the saponification of (*a*) phenyl salicylate, (*b*) benzoic anhydride, and (*c*) nitroglycerol.

Differentiation between Esters and Anhydrides.—Three common classes of compounds contain an oxygen atom uniting two carbon atoms, viz.:

$$R\text{–}CH_2\text{–}O\text{–}CH_2\text{–}R \qquad \text{Ether,}$$

$$R\text{–}C(=O)\text{–}O\text{–}CH_2R \qquad \text{Ester, and}$$

$$R\text{–}C(=O)\text{–}O\text{–}C(=O)\text{–}R \qquad \text{Anhydride.}$$

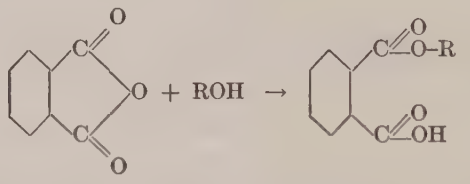
The ethers are stable towards the usual alkali treatment. In the esters, the $-C(=O)-$ structure has greatly weakened the –C–O–C linkage. It is logical therefore to expect that a compound possessing two carbonyl groups joined through oxygen, $-C(=O)-O-C(=O)-$, will be unusually susceptible to hydrolysis. This is true, and we

may therefore differentiate the anhydrides from the esters by (*a*) the great susceptibility of the former type to undergo hydrolysis and (*b*) the fact that the hydrolysis of the former produces no alcohol as a by-product. Very often the hydrolysis of anhydrides may be carried out in the cold with dilute alkali. Esters usually require refluxing with strong alkali, sometimes in alcoholic solution.

It should be remembered, however, that some esters of polycarboxylic acids, such as oxalates and malonates are hydrolyzed very readily. Methyl and ethyl formate, methyl acetate, etc., are also rapidly hydrolyzed in aqueous solution but the boiling-points (below 130°) of the latter compounds exclude the possibility of anhydrides. Explain.

The acyl halides may be considered as mixed anhydrides; they are, however, differentiated from the usual anhydride in connection with the elementary analysis.

A logical method for differentiating an anhydride from an ester is based upon the fact that the anhydride can react with an alcohol to produce one mole of ester and one mole of free acid. An anhydride of a dicarboxylic acid will react to produce an acid ester.

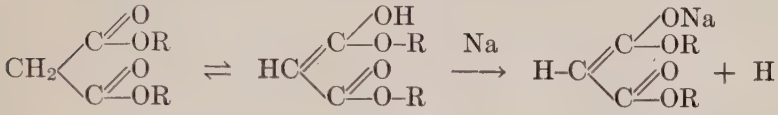


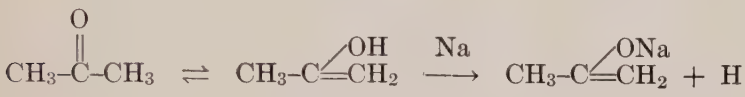
Additional reactions of anhydrides are discussed in the following chapter in connection with the tests for amines. The use of such reactions is reversible, and amines may be used as reagents to test for anhydrides.

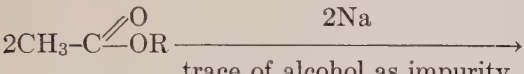
Differentiation between Alcohols and Ethers.—Alcohols may be differentiated from ethers by the usual reactions of the hydroxyl group, viz.:

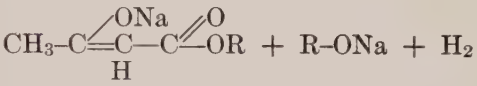
(1) Reaction with metallic sodium,
(2) Reaction with acyl halides and anhydrides,
    (*a*) Acetyl chloride,
    (*b*) Benzoyl chloride,
    (*c*) Other acyl halides,
    (*d*) Anhydrides,
(3) Reaction with phenyl isocyanate.

The most common interfering substance is water. The enolic forms of aldehydes, ketones, and tautomeric esters also possess –OH groups and will respond to some of these tests, particularly to the metallic sodium test. It is partly for this reason that tests for aldehydes, ketones, esters, etc., precede tests for alcohols.

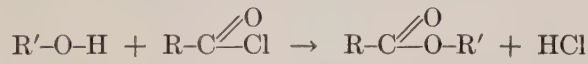


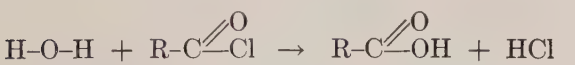






The Use of Acyl Halides or Anhydrides is more satisfactory than that of metallic sodium since the enolic forms of most aldehydes and ketones are not detected by these reagents.





One cc. of the unknown is treated cautiously with 1 cc. of acetyl chloride. The signs of reaction are the evolution of heat, the liberation of hydrochloric acid gas, and the formation of an ester. The fact that esterification has taken place is indicated by the odor of the reaction product after it has been poured into a small amount of water to remove the excess of acetyl chloride; a mere trace of alcohol as impurity in an ether might also be respon-

sible, however, for an ester odor. Change in solubility is another sign of reaction, as is indicated in Table XVII below.

TABLE XVII

Alcohol	Solubility of the alcohol. Grams per 100 grams of H_2O	Solubility of the acetyl derivative. Grams per 100 grams of H_2O
Ethyl	∞	8.0
Propyl	∞	1.5
Isobutyl	10	0.7
n-Butyl	9	0.6
Isoamyl	2.5	0.2

A change in other physical properties, such as conversion of a liquid unknown to a solid derivative, is another indication of reaction. In special instances, the reaction product may be isolated, washed free from acids, and the presence of the acetyl group determined by saponification tests (page 140).

In the acylation reaction, primary and secondary alcohols behave in the normal manner but tertiary alcohols often react to produce halogen derivatives of hydrocarbons.

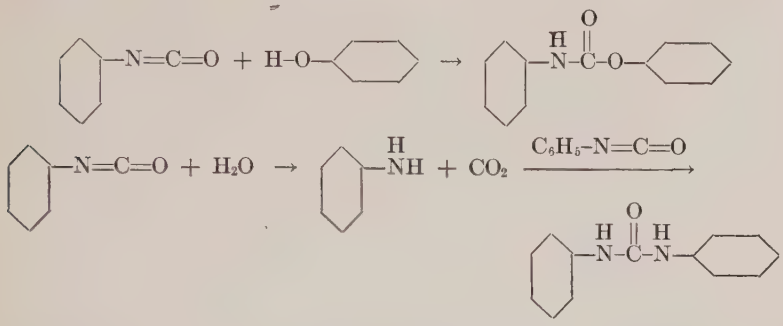
$$\begin{matrix} R \\ R' \\ R'' \end{matrix}\!\!>\!C\text{–}OH + CH_3\text{–}C(=O)\text{–}Cl \rightarrow \begin{matrix} R \\ R' \\ R'' \end{matrix}\!\!>\!C\text{–}Cl + CH_3\text{–}C(=O)\text{–}OH$$

Benzoyl chloride possesses the advantage over acetyl chloride in that it is only very slowly decomposed in cold water and therefore it may be used in detecting alcohols even in aqueous solution, since the –OH group in the alcohol reacts much more rapidly with the acyl chloride than does the –OH group of water. The reaction is usually carried out in aqueous solution containing sufficient alkali to decompose any excess of benzoyl chloride into the water-soluble benzoate. The benzoyl esters formed are insoluble in water.

The substance most frequently interfering with the acetyl chloride test is water. The –OH groups of most phenols act similarly to the alcoholic –OH group. Ammonia, primary amines, and secondary amines react unusually readily with the acyl halides and anhydrides and therefore special precautions must be used in applying the test to nitrogenous compounds.

Phenylisocyanate Test.—Alcohols and phenols react with isocyanates in the manner indicated by the subsequent equations, the latter the more

readily. One of the common reagents used in organic laboratory work is phenylisocyanate.



The presence of moisture interferes with the reaction and the reagent is also sensitive to ammonia and to the amines. With a few exceptions, the usual acyl anhydrides do not react with the enols, whereas phenylisocyanate has found considerable application as a reagent to detect the enolic forms of certain tautomeric compounds.

The Differentiation between Primary, Secondary and Tertiary Alcohols.—Primary, secondary and tertiary alcohols differ greatly in their reaction velocities in esterification with acetic acid; these velocities[1] are approximately as follows: I : II : III : : 40 : 20 : 2. The amount of esterification which has taken place in a given time under standardized conditions therefore is of considerable value in differentiating between the various classes of alcohols. For general qualitative work, it is scarcely adaptable, since several hours are required for the determination.

The Hydrobromic Acid Method.—Most tertiary alcohols react very quickly with 48 per cent hydrobromic acid to give a good yield of alkyl bromide. Secondary alcohols react fairly rapidly when they are refluxed with the hydrobromic acid solution, whereas primary alcohols react slowly upon refluxing but quite rapidly when one mole of H_2SO_4 is used for every two moles of hydrobromic acid.[2]

The Phthalic Anhydride Test.—Phthalic anhydride reacts with primary alcohols when a benzene solution of the two compounds is refluxed. Secondary alcohols react less readily and it is usually necessary to heat the mixture of anhydride and alcohol to a temperature of from 100° to 120°. Tertiary alcohols do not react.

The Victor Meyer Method is adaptable mainly to alcohols of low molecular weight. These alcohols are converted into the corresponding nitro compounds through the iodides. Primary, secondary and tertiary nitro compounds may then be easily differentiated. The tertiary nitro compound does not dissolve in dilute alkali, while the other two members are alkali-soluble, due to their ability to exist in an aci-form. The last two may be

[1] Weyl, Methoden, Part II, p. 756 (1911).
[2] J. Am. Chem. Soc. **42**, 299 (1920).

differentiated by their action towards nitrous acid. The secondary nitro compound forms a nitroso derivative which is no longer soluble in alkali and which usually possesses a characteristic color. The primary nitro compound forms a nitroso compound which is alkali-soluble because of its ability to exist in the isomeric oxime form. Although the Victor Meyer test is rather limited in its application to alcohols, the same reactions are of value for the differentiation between I, II, and III alkyl iodides and I, II and III aliphatic nitro compounds. For this reason it deserves mention here.

Problem 19.—Write equations to illustrate the reactions involved in the Victor Meyer method for the differentiation between I, II and III alcohols. Weyl, p. 753 (1911).

Neutral Compounds of Group I.—Aldehydes, ketones, and alcohols of low molecular weight, together with a few esters, are found in Solubility Group I, since they are soluble in water and also in ether. They will usually, but not always, be met as liquids. When a substance is located in Group I, the aqueous solution of the unknown is immediately tested for acidity, so as to differentiate the neutral from the acidic substances. If the aqueous solution is acid to litmus, a portion of the unknown, about 0.2 g., is titrated with 0.1 N. alkali, using phenolphthalein as an indicator. Small amounts of acid, often inorganic, may be present as impurities and it is important therefore to know approximately the amount of acidity.

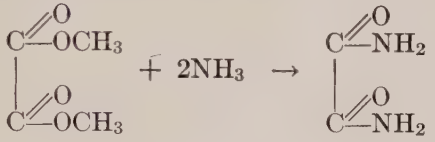
A few esters in Group I will produce acid reactions and this is true of all the water-soluble anhydrides. Upon titration, the former will be neutralized gradually, whereas the water-soluble anhydrides are saponified more rapidly.

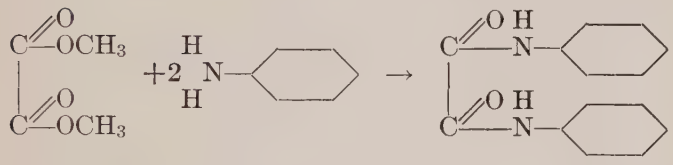
Problem 20.—How many cc. of 0.1 N alkali are required to neutralize (*a*) 0.1 g. of propionic acid, (*b*) 0.1 g. succinic anhydride, (*c*) 0.1 g. aniline sulfate, and (*d*) 0.1 g. methyl oxalate assuming that only one ester group is rapidly saponified? Phenolphthalein is used as the indicator.

The discussion of reactions of neutral oxygen compounds and the order of applying tests in Group V applies directly to the corresponding compounds in Group I, variations being in degree only, since the low molecular weight compounds differ mainly in possessing greater rates of reaction towards the reagent employed. The low molecular weight aldehydes and ketones will react with phenylhydrazine almost instantaneously, whereas a ketone, like

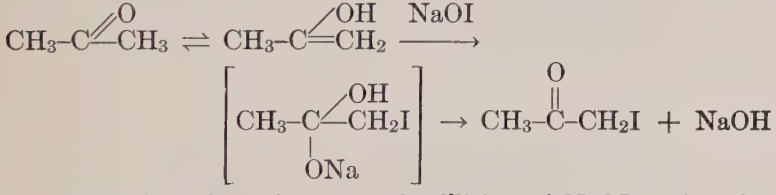
benzophenone, $C_6H_5–\overset{\overset{O}{\|}}{C}–C_6H_5$, reacts comparatively slowly.

Aldehydes of Group I react unusually rapidly with ammoniacal silver nitrate and with fuchsin aldehyde reagent. Similarly, esters and anhydrides undergo hydrolysis more readily than the corresponding classes in Group V, a reaction which is aided partly, of course, by the fact that the compounds are water-soluble. Several esters in this group react so readily with water, ammonia, and the amines, that they might be mistaken for anhydrides by the uninitiated. However, they yield both acids and alcohols upon hydrolysis.

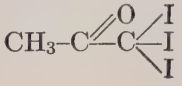




The Iodoform Test.—Compounds in Group I which possess the aceto group $\left(CH_3-C\overset{O}{\diagup\!\!\diagdown}-\right)$ united to either carbon or hydrogen, or compounds which are oxidized to this structure under the conditions of the experiment, will respond to the iodoform test. (Exp. 10, Chapter IX.) A positive test consists in the precipitation of iodoform when a dilute (5 per cent) solution of the unknown is treated with NaOI solution, either in the cold or upon warming to 60° during a few minutes time. The reactions involved are as follows:



Enolization of the ketone and addition of NaOI again takes place and results in the formation of:



a compound unstable in the presence of alkali.

$$CH_3{-}C(=O){-}CI_3 + NaOH \rightarrow CH_3{-}C(=O){-}ONa + CHI_3$$

Problem 21.—Classify the following compounds into two groups, (*a*) those which will respond to the iodoform test, and (*b*) those which will fail to yield iodoform under the usual experimental conditions:

(1) acetone,
(2) methyl alcohol,
(3) ethyl alcohol,
(4) propyl and isopropyl alcohols,
(5) acetic acid,
(6) isobutyl alcohol,
(7) secondary butyl alcohol
(8) acetaldehyde,
(9) propionaldehyde,
(10) levulinic acid,
(11) pyruvic acid,
(12) acetoacetic ester,
(13) diethyl ether.

Acidic Compounds.—The main acidic compounds containing only the elements C, H, and O are the carboxylic acids and the phenols. These compounds are found mainly in Group IV, although the water-soluble members will be found divided between Groups I and II. A relatively small number of phenols belong to the alkali-insoluble class and are liable to be classified in Group V (see Chapter II, problem 3).

The majority of phenols are feebly acidic in comparison with the carboxylic acids; the latter may be titrated quantitatively in aqueous solution using phenolphthalein as an indicator, but this is not true of the phenols. Methods of classification, such as the following, have been proposed, but are so obviously open to exceptions that a brief discussion is necessary.

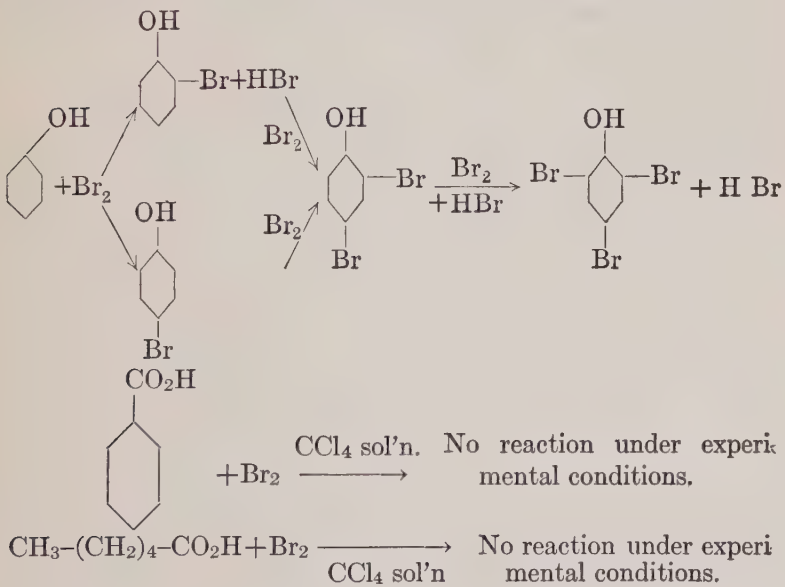
(1) Phenols	Soluble in alkali but precipitated upon saturating the solution with carbon dioxide. Insoluble in $NaHCO_3$ solution.
(2) Weak Carboxylic Acids (not negatively substituted)	Soluble in $NaHCO_3$ solution but insoluble in sodium formate solution.
(3) Strong Carboxylic Acids, particularly dicarboxylic acids, nitro carboxylic acids, etc. Sulfonic Acids, etc.	Soluble in sodium formate solution.

The above classification may lead to error because it does not take into consideration the water-solubility of the individual

compounds. The partition of a base between two acids is controlled not only by the respective strengths of the acids, but also by their concentrations. In substances very sparingly soluble in water, the concentration of the dissolved substance is greatly limited and this is the reason that certain acids, although strong acids, are precipitated by carbon dioxide; on the other hand, many phenols are sufficiently soluble in water to fail to precipitate with carbon dioxide. This method of differentiation must be used, therefore, with proper appreciation of its limitations.

Certain other classes of acidic compounds, such as imides, sulfonamides, etc., when only sparingly soluble in water, can be precipitated from their sodium salts by means of carbon dioxide.

Differentiation between Phenols and Acids.—Although the above solubility differentiation for these two classes of compounds possesses a certain value when applied in the light of the limitations, a more valuable method of differentiation is available because of the fact that the phenol group increases enormously the velocity of bromine substitution in the benzene ring. The sign of reaction in carbon tetrachloride is the evolution of copious amounts of hydrobromic acid. When the test is conducted with a dilute aqueous solution of a phenol, the sign of reaction is the formation of a sparingly soluble bromine substitution product.



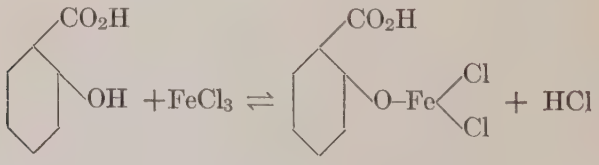
Discussion of the Reaction and of Its Limitations.—The reaction between phenol and bromine takes place very readily at room-temperature, the second and third atoms of bromine substituting almost as readily as does the first to produce tribromophenol. Most substituted phenols also show great reactivity, as is indicated below, but replacement of the H of the phenolic —OH group by alkyl or acyl radicals decreases the reactivity.

Problem 22.—Write the reactions between bromine and (*a*) salicylic acid, (*b*) *p*-nitrophenol, and (*c*) fluorescein.

The phenolic structure adds to the ease of substitution into the benzene ring, not only of bromine, but of other groups, such as chlorine, nitro, sulfonic etc.; it also tends to the instability of the aromatic nucleus toward permanganate oxidation. In order to oxidize side-chains in the presence of the phenol group, it is necessary to protect the latter. How? The amine group also increases the ease of substitution in the aromatic nucleus and this fact must be remembered in testing basic compounds. Bromine in carbon tetrachloride may also attack certain aldehydes, ketones and esters, both in the aliphatic and the aromatic series. This is true especially among the types which exist to a considerable extent in the enolic forms, since the mechanism of substitution in such cases is no doubt first an addition of bromine to the enolic form, followed by the elimination of hydrobromic acid. The use of carbon tetrachloride as a diluent possesses the advantage in that bromine is more readily handled, it acts as a solvent for the organic compounds, hydrobromic acid is insoluble in this solution, and the reaction velocity is somewhat lowered. A number of hydrocarbons which react readily with liquid bromine react only slowly in carbon tetrachloride solution.

Phenols having para or ortho positions unoccupied couple readily with diazonium compounds; this is simply another example illustrating the ease of substitution.

The Ferric Chloride Phenol Test.[1]—Many phenols give typical blue, green, purple, or red colors when a drop of ferric chloride is added to a dilute aqueous solution of the unknown. A number of phenols which do not give this test readily are found to respond when tested in alcoholic solution. Among the carboxy derivatives of phenol, those having the carboxyl group ortho to the phenolic hydroxyl, as in salicylic acid, respond with a typical deep purple color, but many compounds with the carboxyl group in the meta or para position fail to respond to the test.



[1] Cf. Ann. **323**, 10, 20 (1902).

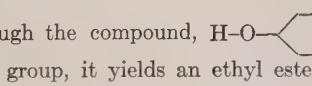
Typical enols, which, like the phenols, possess an –OH group united to the unsaturated carbon, give deep red colorations, a fact which has been used in connection with the investigation of tautomeric substances. α-Hydroxy acids may produce a yellow color and some common aliphatic acids, like acetic, give the well-known red color under suitable experimental conditions. Example: The qualitative test for acetic acid in inorganic chemistry.

Other Reactions of the Phenol Group.—The phenolic group possesses many reactions in common with the alcoholic group; thus, acyl chlorides react readily with most phenols to form esters. Diphenyl carbamine chloride, $(C_6H_5)_2N-C(=O)-Cl$, a common reagent used in preparing derivatives of the phenols, is more reactive toward the phenolic than toward the alcoholic group and this is true also of alkyl sulfates which react readily with the sodium salts of phenols to produce alkyl ethers. Several of the common phenols may be condensed with phthalic anhydride to produce phthaleins.

Reactions of the Carboxyl Group.—Important reactions of the carboxyl group, $-C(=O)-O-H$, are (*a*) salt formation, (*b*) esterification, (*c*) formation of acyl halides, (*d*) formation of amides, and (*e*) loss of CO_2.

Salt formation is typical of all the compounds listed in Group IV. A partial differentiation between the various members of this group has already been considered in connection with the differentiation of the carboxylic and sulfonic acids from the weakly-acidic substances upon the basis of solubility in $NaHCO_3$ solution. Acidic compounds should be titrated with standard alkali (p. 138) and the neutral equivalents determined. The carboxylic acids will give practically the same neutral equivalents whether the titrations are carried out in aqueous or alcoholic solution. Feebly acidic compounds will show an abnormally high neutral equivalent, especially when titrated in aqueous solution.

Important reactions, such as esterification, the formation of acyl halides and amides, anhydride formation of certain dicarboxylic acids, and related reactions will be illustrated in the section dealing with the preparation of derivatives.

Problem 23.—Although the compound,  , does not contain a carboxyl group, it yields an ethyl ester when refluxed with alcoholic HCl. By means of equations, write the reactions involved.

Volatility Constants of Aliphatic Acids.—The mono carboxylic derivatives of the paraffin hydrocarbons up to and including those containing six carbon atoms are readily volatile with water vapor. These acids differ very widely in their degrees of volatility when diluted solutions are subjected to distillation, and accordingly Du Claux[1] has based upon this fact a quantitative method for the

[1] Ann. chim. phys. [5] **2**, 289 (1874); Analyst **20**, 193, 217 (1895); J. Am. Chem. Soc. **39**, 731, 746 (1917).

estimation of individual acids and for some of their mixtures. Although open to certain objections from the quantitative standpoint, the method is of considerable value in connection with qualitative organic analysis, and is therefore presented in Chapter IX, Exp. 16.

CHAPTER IV

CLASSIFICATION REACTIONS OF THE SIMPLE NITROGEN AND SULFUR COMPOUNDS

BASIC NITROGEN COMPOUNDS

With a few exceptions, the basic organic compounds contain nitrogen. When solubility tests have placed a compound in Group III but elementary analysis has failed to prove the presence of nitrogen, it will be advisable to repeat the tests for the elements. The most important basic nitrogen compounds are the amines; the discussion in Chapter II has dealt with the effect of various substituting groups upon the basicity of the amine group and this section (pp. 19–21) should be reread in connection with the present discussion.

The first test to be applied to basic compounds is the acylation test: Ammonia, primary amines, and secondary amines are readily acylated, whereas tertiary amines usually undergo no similar reaction although in the latter case addition products with acyl halides may be formed.[1]

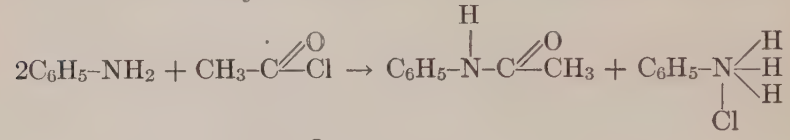
The most important acylating agents used in the laboratory are:

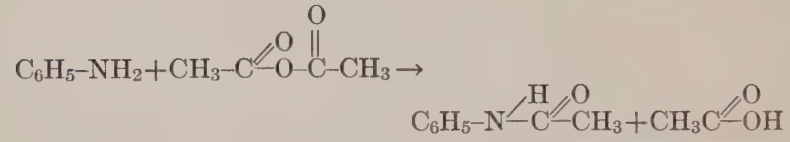
(1) Acetyl chloride and acetic anhydride,
(2) Benzoyl chloride,
(3) Benzenesulfonyl chloride,
(4) Phthalic anhydride.

As has already been pointed out in Chapter III, the acyl halides and anhydrides react readily with the hydroxyl groups of alcohols and phenols. This fact must be kept in mind in connection with tests for amines. Acid chlorides of low molecular

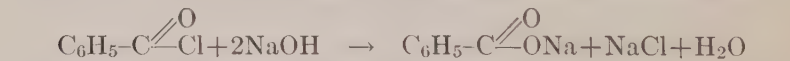
[1] Dehn, J. Am. Chem. Soc. **36**, 2091 (1914). At higher temperatures, an alkyl group may be replaced by the acyl group. Ber. **19**, 1947 (1886).

weight, particularly acetyl chloride, react readily with water. Benzoyl chloride, benzenesulfonyl chloride, and similar derivatives, however, may be safely used to test for amines in the presence of water. Why?





In the above equations, it should be noted that acetyl chloride does not convert aniline completely into the acetyl derivative since the by-product, aniline hydrochloride, is formed and this does not act readily with the reagent. On the other hand, with acetic anhydride the amine is converted quantitatively into the acyl derivative and therefore this latter reagent is of more importance in connection with the preparation of derivatives. It is also of value in quantitative estimations of the amine group, the excess of acetic acid which remains after the reaction being determined volumetrically. Benzoyl chloride, benzenesulfonyl chloride, and other acyl halides that may be used in aqueous solution may also convert the amine completely into an acyl derivative for the reason that they are usually used in the presence of alkali which will combine with the hydrochloric acid generated in the reaction. When benzoyl chloride is used, a small amount of benzoic acid may be formed, due to the following side-reaction:

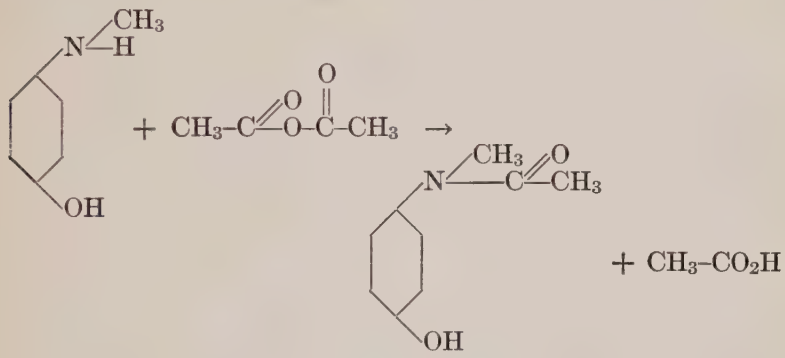


The slight excess of benzoyl chloride that is generally used in the reaction must be destroyed completely in order to prevent it from contaminating the derivative. The benzoic acid, however, remains in the solution as sodium benzoate, whereas the benzoyl derivative of the amine is insoluble in alkali unless some acidic group like carboxyl is simultaneously present.

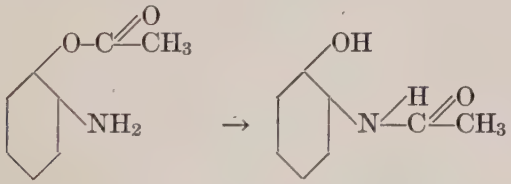
Problem 24.—Criticise the following laboratory test: One-half cc. of the unknown (basic compound, b.p. 190°–195°) was treated with an equal volume of acetyl chloride. A violent reaction took place and a solid deriva-

tive was formed. A portion of this solid was removed from the test tube and transferred to a clay-plate in order to remove most of the adhering oil and finally was washed by several applications of ether. The snow-white crystals remaining failed to check in melting-point with the acetyl derivatives of any amine boiling in the neighborhood of 190°–195°.

The acyl halides and anhydrides react with the amine group more readily than with the hydroxyl group. For example, when an amino phenol is treated in water solution with one mole of acetic anhydride, the acetyl group will substitute the amine hydrogen atom far more rapidly than the hydrogen of the hydroxyl group.



In ortho aminophenols, acyl groups may migrate from the oxygen to the nitrogen atom.



This is simply an illustration of the reaction of an ester with an amine to form an amide, except that in the above case the ester and the amine groups are located in the same molecule.

Differentiation between the Various Classes of Amines.—*A.* Primary, secondary, and tertiary amines may be differentiated by a combination of the acetyl chloride and the isonitrile tests.

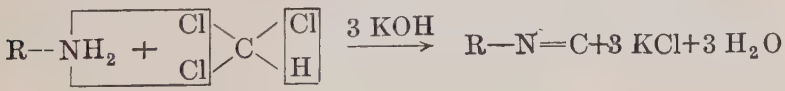


TABLE XVIII

UNKNOWN + ACETYL CHLORIDE

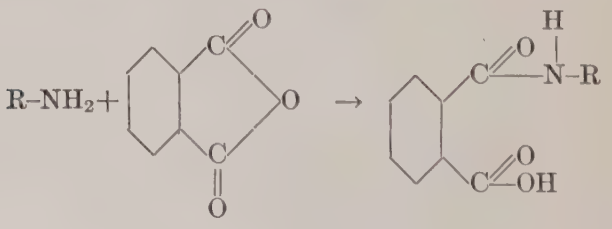
Positive reaction. I or II amine. Heat original amine with $CHCl_3$ and alcoholic potash		No reaction. III amine
Positive reaction. I amine	No reaction. II amine	

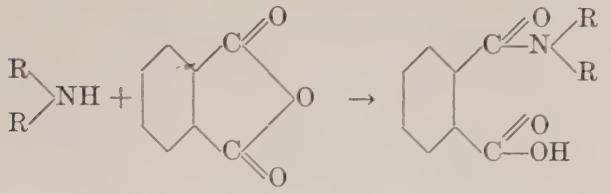
In this test, the formation of an isonitrile is detected by the extremely disagreeable odor that is typical of this class of compounds. The test is not very satisfactory because it is too delicate and consequently most secondary amines, which usually contain traces of primary amines, will respond to the test. Exceptions are also found, especially among the amines of high molecular weight.

B. Benzenesulfonyl chloride (and other aryl sulfonyl chlorides) possess an advantage over the usual acyl chlorides of the acetyl or benzoyl type in that the sulfonyl derivatives of primary amines may be differentiated from the corresponding derivatives of secondary amines due to the solubility of the former in alkali. This reaction will be discussed further in Chapter XII in connection with its application to mixtures.

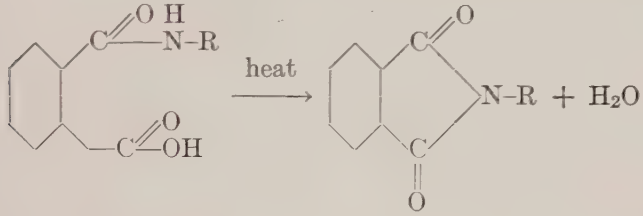
Problem 25.—Write the structural formulas for sulfonyl derivatives of I and II amines and explain why these derivatives behave differently in their reactions with dilute aqueous NaOH solution.

C. Phthalic Anhydride reacts with many I and II amines very readily, even without heating; III amines show no reaction.





The derivative of the I amine may be differentiated readily from the other. When heated slightly above its melting-point a dehydration reaction occurs with the formation of a product no longer soluble in alkali.



The reactions of the amines discussed above, with the exception of the isonitrile test, are of importance not merely for the classification of compounds but also for the preparation of solid derivatives and in some instances for the examination of mixtures. Such reactions, which serve simultaneously as classification and as identification reactions, are ideal for the purposes of organic analysis.

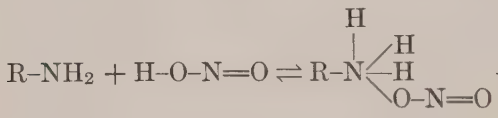
The Behavior of Amines Towards Nitrous Acid is also occasionally of value to differentiate between the three classes of amines. In these reactions, primary amines behave somewhat differently from the secondary amines. Ammonia also reacts, and, indeed, we have here simply an example of the method of preparing nitrogen which was studied in inorganic chemistry.

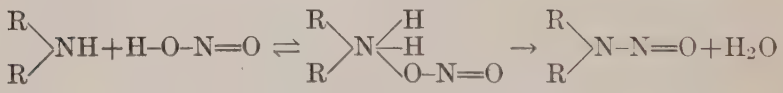
$$NH_3 + HNO_2 \rightarrow \begin{matrix} H & H \\ \diagdown & \diagup \\ HN & -O-N=O \\ H & \end{matrix} \rightarrow N_2 + 2H_2O$$

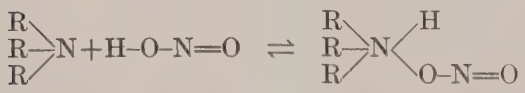
Primary aliphatic amines also form nitrites which decompose in a manner analogous with the decomposition of ammonium nitrite except that in this instance nitrogen gas *and an alcohol* are formed. This decomposition is not as rapid, however, as one

might wish for qualitative tests. When the primary amine group is in the alpha position in respect to a carboxyl group, as in many of the common amino acids, a very rapid reaction with nitrous acid takes place with a practically quantitative evolution of nitrogen gas. The Van Slyke method for the quantitative determination of the alpha-amino acids is based upon this reaction. The $-NH_2$ group of amides will also react with the formation of an acid and nitrogen gas. This reaction is also less rapid than is the reaction with the alpha-amino acids.

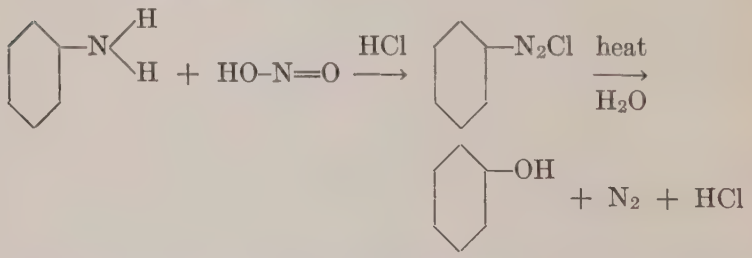
Secondary aliphatic amines react with nitrous acid to give nitroso derivatives which are practically neutral substances and insoluble in water unless the amine is of very low molecular weight. Tertiary aliphatic amines do not react with nitrous acid under the usual conditions except to the extent of salt formation.







In the aromatic series, we find that primary amines react extremely readily in the cold to form intermediate water-soluble products known as diazonium compounds. When the diazonium solution is warmed, decomposition takes place with the formation of nitrogen gas and a phenol.



These diazonium compounds are extremely valuable in synthetical work, since the diazonium group may be replaced with a large

variety of other groups, such as Cl, Br, I, CN, H, OC_2H_5, NO_2, SO_2H, etc. These special applications of the diazonium compounds are seldom used in qualitative work since the simpler reactions are usually sufficient.

In addition to replacement reactions, the diazonium compounds readily undergo coupling reactions with many phenols and amines. These reactions, which are of great technical importance, are also of value in both qualitative and quantitative organic work.

Problem 26.—What reagents and conditions are used to replace the diazonium group with (*a*) chlorine, (*b*) $-C\equiv N$, and (*c*) hydrogen? How may a diazonium compound be converted into a hydrazine?

Problem 27.—Write the equations to illustrate the coupling reactions of diazonium compounds with phenols and with tertiary aromatic amines.

Secondary aromatic amines behave as do the corresponding amines in the aliphatic series; they form nitroso compounds which are neutral substances and only sparingly soluble in water. They separate from solution when the amine hydrochloride is treated with sodium nitrite solution. Occasionally, when these nitroso compounds are solids, they may be used for derivatives.

The Tertiary Amines.—This class of amines differs from ammonia and the primary and secondary amines in its non-activity with acyl halides and anhydrides.

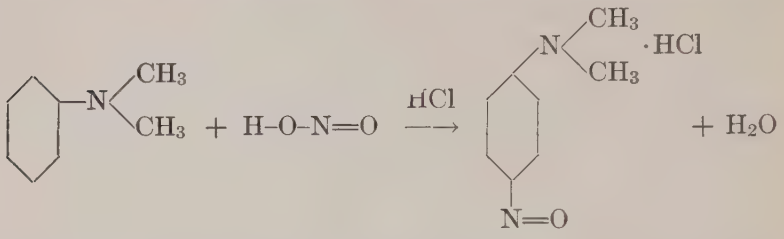
Many amines, including the tertiary type, form double salts with such reagents as chloro-platinic acid, picric acid, etc. These derivatives are of importance in analytical work in connection with identification tests. The formation of picrates, however, is not peculiar to the amines; in fact, such derivatives may be prepared even from the hydrocarbons of the naphthalene and anthracene series.

Tertiary amines may add alkyl halides and form quaternary ammonium compounds which are often solids with definite melting-points. The alkyl iodides are usually applied for this purpose.

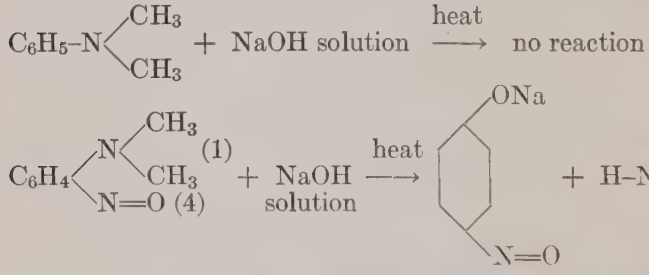
$$R\text{–}N\begin{matrix}R\\R\end{matrix} + R'X \rightarrow R\text{—}N\begin{matrix}R\\R\\R'\\X\end{matrix}$$

An important reaction of *aromatic* tertiary amines consists in the formation of nitroso derivatives when the amine salt in acid

solution is treated with sodium nitrite. This reaction is typical mainly when the para position to the amine group is unoccupied.

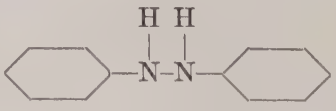


Since in the above reaction-product the nitroso group is on carbon and not on nitrogen, we obtain a compound which is still basic and thus differs from the nitroso derivatives of aromatic secondary amines. The introduction of the nitroso group leads to instability of the molecule towards alkali.



An important class of tertiary amines is represented by compounds of the pyridine and quinoline types. Although these classes are considered as aromatic in character, the basic N atom does not add to the case of substitution into the nucleus. These cyclic amines behave more like the tertiary aliphatic amines since they do not form nitroso derivatives, and they do not couple with the diazonium compounds. Addition products with the alkyl halides are formed very readily.

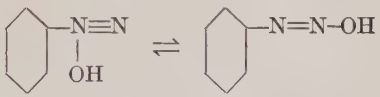
Other Basic Nitrogen Compounds.—The hydrazines, unless negatively substituted on the nitrogen, are typical organic bases. Phenylhydrazine (C_6H_5–NH–NH_2) is only sparingly soluble in water but dissolves readily in dilute HCl. When a second aryl group is introduced,



we obtain a hydrazo compound which is practically neutral. Hydrazines possessing the structures $R-\overset{H}{\underset{|}{N}}-NH_2$ and $R-\overset{O}{\overset{\|}{C}}-\overset{H}{\underset{|}{N}}-NH_2$, are detected by using benzaldehyde or some other convenient carbonyl compound as a reagent.

Problem 28.—Write the equation for the reaction between (*a*) vanillin, and NH_2-NH_2, (*b*) hydrazobenzene and aqueous HCl.

The diazonium hydroxides are fairly strong bases. These compounds and their salts have been discussed in connection with the reactions of primary aromatic amines. Although very important in organic work, the diazonium compounds are rarely found among the compounds requiring identification. This is easily understood when we recall that most of them are stable in solution only at comparatively low temperatures. In the form of dry solids, most of the salts are highly explosive.



Benzene diazonium hydroxide

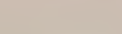
Quaternary ammonium hydroxides, $(R)_4N-OH$, are very strong bases like the highly ionized inorganic hydroxides. They are seldom met, and then usually as chlorides or sulfates. They are manipulated best in the form of platinic chlorides.

Carbamide (urea) forms salts with one mole of acid ($NH_2 \cdot CO \cdot NH_2 \cdot HNO_3$), but in water solution they are mostly hydrolyzed and the acid may be titrated, even with phenolphthalein as an indicator. The enzyme preparation "urease" is convenient for the identification and estimation of urea.

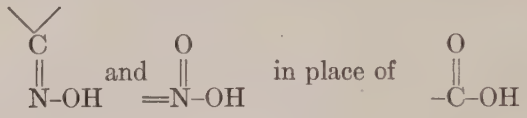
Amidines, some guanidine derivatives, imino-ethers, etc., are not sufficiently common to require individual attention here. Oximes, when water-insoluble, occasionally give evidence of basic properties by increased solubility in dilute HCl.

Problem 29.—Write the equation for the action of sodium hypobromite in alkaline solution upon (*a*) benzamide, and (*b*) urea.

Acidic Nitrogen Groups.—When a hydrogen of ammonia is replaced by an acyl group of a strong acid (sulfonic acid), an acidic amide is formed. A similar result is obtained by introducing two acyl groups derived from carboxylic acids, thus resulting in the formation of an imide (page 20). An examination of the tautomeric (lactam and lactim) formulas for these compounds suggests an analogy with the structure of the car-

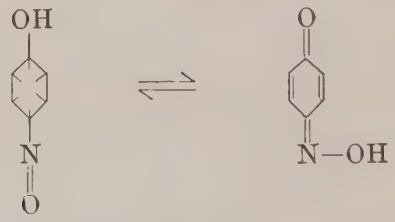
boxyl groups, since here also an –OH group is linked to a carbon which is unsaturated; viz.: in place of  .

Similarly, there are nitrogen groups which may be considered as related to the carboxyl group but which possess the nitrogen (tri- or pentavalent) replacing the carbon of the carboxyl; e.g.,



Compounds containing these groups are acidic, although in the case of oximes, very feebly acidic. They are often met in a different guise, the above formulas representing simply the "aci" form of primary and secondary nitroso and nitro compounds. See page 22 and Problem 4.

Tertiary nitroso and nitro compounds do not exhibit this type of isomerism except in special instances in the aromatic series when, due to the presence of certain other groups, the derivative may exist in the form of a quinone-like compound.

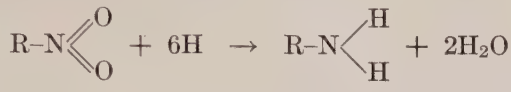


The acidic nitrogen groups may be subjected to the same class reactions which are used for the neutral nitrogen groups and a separate discussion will therefore be unnecessary.

Neutral or Indifferent Nitrogen Groups.—The four most common indifferent nitrogen groups are the nitro, azo, nitrile, and amide. The following discussion will deal also with a number of other analogous groups that are met only occasionally in elementary analytical work. These classes of compounds may be arranged conveniently into two sub-groups:

(*a*) Easily reducible type,
(*b*) Easily hydrolyzable type.

The nitro and azo compounds are readily reduced by acid reducing agents to yield primary amines.



$$R\text{–}N=N\text{–}R' + 4H \rightarrow R\text{–}NH_2 + R'\text{–}NH_2$$

In the above reductions, the amines are present in the form of salts of the inorganic acid used. In the iron reduction method, however, where only a very small amount of acid is used as a catalyzer, the amines are present mostly as free amines, and for this reason in the reduction of fairly volatile substances provision must be made to prevent loss either of amine or of the initial material.

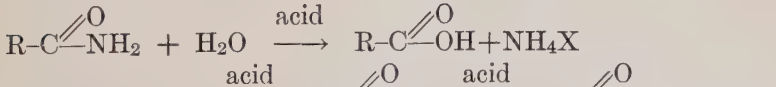
The reducing reagents which are commonly used in the laboratory are:

(*a*) Tin and aqueous HCl,
(*b*) Iron powder and 5 per cent iron chloride and water,
(*c*) Zinc and neutral salt solutions,
(*d*) Sodium amalgam,
(*e*) Stannous chloride in HCl solution,
(*f*) Zinc and acid.
(*g*) Zinc and alkali.

As will be seen from the subsequent discussion (see also Problem 35), the reaction of the medium exerts a great effect upon the particular reduction products to be formed.

Problem 30.—The reducing agents above are given in the order of importance for laboratory work in qualitative analysis. Explain how and why this order differs in technical manufacturing work.

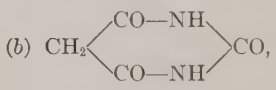
Amides and nitriles may be readily hydrolyzed to produce the corresponding acids together with ammonia or, in the case of certain amides, substituted ammonia. To be sure, the amides and nitriles may also be reduced to amines, especially with sodium in alcoholic solution; with acidic reagents the hydrolytic reaction is, however, the prominent one and the one adaptable for analytical purposes.



The hydrolysis of amides and nitriles may be conducted not only in acid solution but also in the presence of alkali. When dealing with substances soluble in water only with difficulty, it is customary to use alcohol as a solvent. In the latter instance, in connection with acid hydrolysis, the organic acid formed in the reaction is partially converted into an ester, whereas ammonia, or a substituted ammonia, will be present in the form of a salt with the inorganic acid used. When the hydrolysis is conducted in the presence of alkali, the organic acid is present as the sodium or potassium salt, whereas the amine is liberated and, if volatile, may be lost when the reaction mixture is refluxed. Type experiments are illustrated in connection with the laboratory work, page 146.

Problem 31.—Write the equations for the acid hydrolysis of

(*a*) $C_6H_5 \cdot NCH_3 \cdot COCH_3$,

(*b*)  ,

(*c*) $C_6H_5 \cdot CO \cdot NH \cdot CH_2CO \cdot NH \cdot C_6H_5$.

In which reaction is a gas evolved?

Problem 32.—Write the equations and state the experimental conditions for

(*a*) the conversion of an amide into a nitrile,

(*b*) the formation of an amide from an ester.

Problem 33.—Write type formulas for compounds belonging to each class listed in Table XIX under Groups A, B, and C.

Analytical Attack of Indifferent Nitrogen Compounds

Many of the types in Subgroup A represent colored compounds and the few individual members which are not colored when pure are often contaminated with colored impurities. The simple nitro and azoxy compounds are usually light yellow or cream colored, whereas the azo compounds are more highly colored. Additional substituents, for example, amine groups, will deepen the color of nitro compounds. Many simple nitroso compounds are green.

TABLE XIX

Sub-group A. Easily reduced	Sub-group B. Easily hydrolyzed	Sub-group C. Resistant to reduction and hydrolysis
Nitro	Amides	Some negatively substituted amines
Azo	Nitriles	Certain imides
Nitroso	Imides	Many sulfonamides
Azoxy	Derivatives of aldehydes and ketones:	Certain heterocyclic types
Hydrazo	(*a*) Hydrazones	
	(*b*) Oximes	
	(*c*) Semicarbazones	
	(*d*) Osazones	
	(*e*) Aldehyde amine derivatives	
	(*f*) Cyanohydrins	
	Isocyanates	

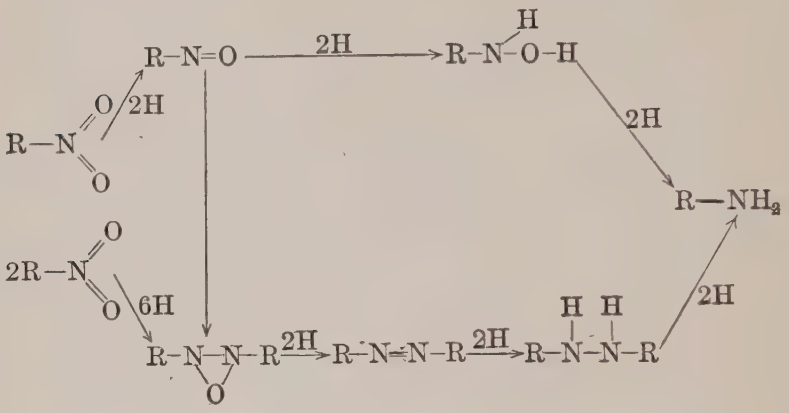
If a given unknown containing indifferent nitrogen is a colorless compound, it is advisable to apply first the hydrolysis test for Subgroup B. On the other hand, colored compounds should be subjected to reduction tests before resorting to those involving hydrolysis. Often a combination of the two tests is advisable, alkaline hydrolysis being resorted to when no definite results are obtained by acid hydrolysis.

With the exception of the nitro and hydrazine compounds, practically all of these compounds may be quantitatively analyzed for nitrogen by the Kjeldahl method. The nitro compounds may, of course, be utilized also in such an analysis following slight modifications from the usual method of analysis.

Discussion of Subgroup A.—The nitrogen compounds in this class may all be reduced to amines by means of acid reduction methods, but they differ considerably in ease of reduction. Further differentiation within the subgroup may often be made by the choice of modified methods of reduction. In many instances the order of reduction is as follows: Nitroso, azoxy, nitro, and azo, the first being reduced most readily. This order differs, however, in regard to the character of the reducing reagent and is modified greatly by the solubility of the compound. In order

to hasten the reduction of sparingly soluble compounds, alcohol is often added.

The inter-relation between these compounds is shown in the following diagram:



The nitro, azo, nitroso, and azoxy compounds may all be reduced to the hydrazo stage by means of zinc dust and alkali in the presence of alcohol. In this reaction, however, the azoxy compounds may often be differentiated from the azo, due to the fact that the former are reduced more readily and upon reduction go through the deeply-colored azo stage.

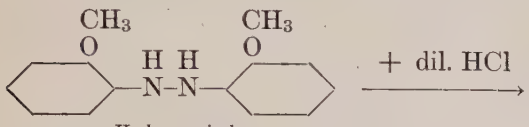
Many nitroso and nitro groups can be reduced by zinc and water in the presence of a small amount of a salt like ammonium chloride as a catalyzer to form hydroxylamine derivatives which readily reduce ammoniacal silver nitrate.[1] The nitroso group may be differentiated by oxidation (HNO_3) to the nitro stage.

Problem 34.—What is Liebermann's Nitroso Reaction? (Mulliken II, 30 (1916).

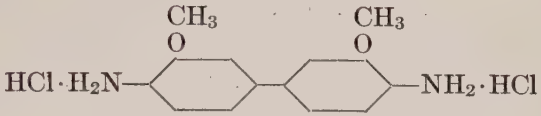
Hydrazo compounds may be oxidized back to the azo stage by passing air into the solution of the compound in alcoholic alkali solution. In glacial acetic acid, 30 per cent hydrogen peroxide gradually oxidizes both hydrazo and azo compounds to the azoxy compounds.

[1] Cf. Mulliken II, 32 (1916).

Several of the types mentioned in the above table are easily affected by treatment with strong acids. This is especially true of the hydroxylamine, nitroso, and hydrazo compounds.



Hydrazoanisole



Dianisidine HCl (*pp'*-di-amino-*mm'*-dimethoxy-diphenyl)

Problem 35.—What products are formed when aryl nitro compounds are reduced with zinc in

(*a*) neutral solution,
(*b*) alkaline solution,
(*c*) acid solution?

How may a similar variety of products be prepared by electrolytic reduction?

Problem 36.—What is formed when sodium methylate acts as a reducing agent on nitrobenzene? Will reduction take place when hydrogen gas from a Kipp generator is passed into boiling nitrobenzene?

In this series of indifferent nitrogen compounds, it is not essential, however, that an unknown be limited to one individual class before proceeding with the work; the identification of the products obtained by reduction or hydrolysis together with the physical constants and other properties of the original unknown, will serve to simplify the procedure greatly.

Problem 37.—In a manner analogous with the explanation of the benzidine rearrangement, explain the formation of *p*-aminophenol from phenyl hydroxylamine and sulfuric acid. What is the semidine rearrangement?

Problem 38.—Hydrazo compounds are colorless. Why do the samples met with usually possess a yellow color. How can we explain that nitrosobenzene is green only when in the liquid or vapor phase? What suggestion can be given for the deepening of color when the nitrophenols are converted into their salts?

Discussion of Subgroup B.—With the exception of formamide, the common amides are solids with fairly high melting-points and usually limited solubility in ether and benzene. The nitriles of the

corresponding acids are generally liquids or low-melting solids unless several $-C\equiv N$ groups are present. The fact that the nitriles may yield amides as intermediate products in their hydrolysis to acids can serve as a method of differentiation. The nitriles will yield ammonia upon complete hydrolysis, whereas amides may be derived from primary and secondary amines as well as from ammonia.

The various nitrogenous derivatives of aldehydes and ketones are usually detected by the products formed by acid hydrolysis. The corresponding carbonyl compounds may be isolated often, and sometimes the nitrogenous products as well. By sodium reduction many of these compounds yield amines, but this reaction is of minor analytical importance.

Problem 39.—Given the phenylhydrazone of methyl ethyl ketone, recover the ketone as such and the phenylhydrazine in the form of its benzaldehyde derivative.

Problem 40.—Two oximes of benzaldehyde are known. Explain this case of isomerism. Do both oximes yield nitriles with acetic anhydride? What is the Beckmann Rearrangement of ketoximes?

Discussion of Subgroup C.—The di- and tri- aryl amines (negatively substituted amines) are practically neutral substances, and naturally are not affected by the usual hydrolytic treatment. Aromatic amines with ortho nitro groups are very feebly basic; when heated with alkali, ammonia is gradually liberated. (Cf. equations, page 66.)

The imides are often met among the acidic substances, but when the hydrogen of the $>NH$ group is replaced with a radical they become neutral. Such compounds, particularly when derived from cyclic structures of the phthalimide and saccharine types, are hydrolyzed only with difficulty under the conditions of the usual experiment. They are placed, therefore, in Subgroup C. Their hydrolysis is usually carried out by heating with HCl to a temperature of approximately 200° in a sealed tube. The sulfonamides, also, are resistant to hydrolysis, and most of them may be placed in Subgroup C. They are acidic substances unless both the hydrogens of the $-NH_2$ group have been replaced by radicals. Certain heterocyclic types, for example, the purine derivatives, although possessing the amide structure, are less susceptible to hydrolysis because of the greater stability given by the ring structure.

The Sulfur Compounds

The main classes of sulfur compounds to be considered are:

Thiols (mercaptans and thiophenols),
Sulfides, including cyclic sulfides,
Disulfides,
Sulfoxides,
Sulfones,
Sulfinic Acids,
Sulfonic Acids and derivatives,
Esters of sulfuric acid,
Sulfates of organic bases, and
Sulfite addition-products of carbonyl compounds.

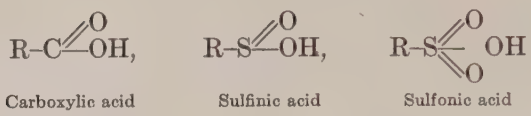
A glance at the formulas for the above types will emphasize the close relationship between oxygen and sulfur; thus the thiols, sulfides, and disulfides are analogous with the oxygen compounds, alcohols, ethers, and peroxides, respectively. Alcohol-like and phenolic types, are found among the thiols just as with the corresponding oxygen compounds. The analogy may be carried to additional examples. For instance, carbon oxysulfide and carbon disulfide are related to carbon dioxide: $C{=}O$, $C{=}S$, $C{=}S$. Related to the carboxylic acids are found compounds in which one or both of the oxygens of the carboxylic group are replaced by sulfur:

$$R{-}C{=}O{-}OH, \qquad R{-}C{=}S{-}OH, \qquad R{-}C{=}O{-}SH, \qquad R{-}C{=}S{-}S{-}H$$

In general, these sulfur compounds possess the reactions of the corresponding oxygen compounds plus the reactions conveyed by the ability of sulfur to assume valences of four or six.

In a second type of sulfur compounds, sulfur is found usurping the place of carbon; for example, related in structure to the ketones are the sulfoxides and sulfones, and related in structure to the carboxyl group are the sulfinic acids. Since sulfur may possess a variable valence, it may give rise also to sulfonic acids which bear the same relation to the sulfinic acids that sulfuric does to

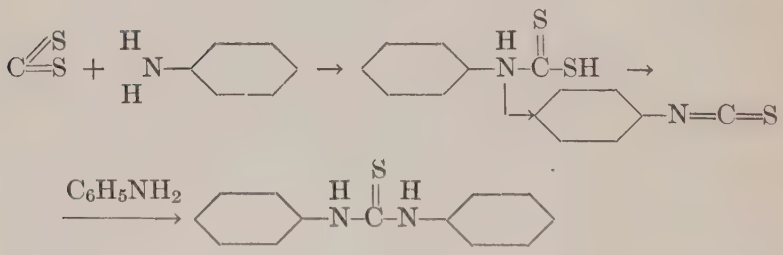
sulfurous. These relationships are indicated in the following formulas:



Carboxylic acid Sulfinic acid Sulfonic acid

With the exception of the sulfonic acids and the sulfates, the above sulfur compounds are of importance only in a few special cases, and a detailed discussion of individual classes is therefore inadvisable in an elementary course. The derivatives of sulfonic acids, such as the sulfonyl chlorides, amides, and imides are of considerable importance in qualitative work.

Carbon Disulfide possesses the ability to form addition products: thus



The former reaction is of technical importance in the manufacture of viscose and the latter is valuable both in the laboratory and in the industries. A corresponding reaction with phenylhydrazine is of value in preparing a derivative of carbon disulfide.

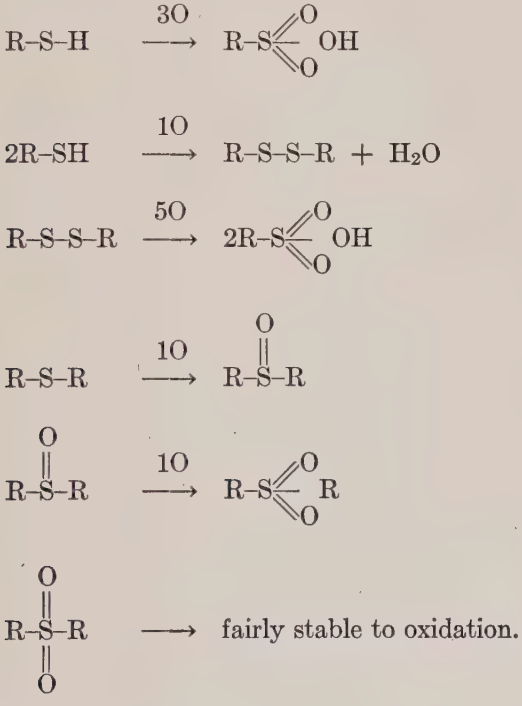
The Thiols and Sulfides are chiefly liquids with penetrating, disagreeable odors. With salts of heavy metals, such as mercuric chloride, the former yield salts and the latter double salts.

$$R\text{–}SH + HgCl_2 \rightarrow (R\text{–}S)_2Hg$$

$$R\text{–}S\text{–}R + HgCl_2 \rightarrow R\text{–}S\text{–}R \cdot HgCl_2$$

Those thiols (mercaptans) related to the alcohols are scarcely acidic enough to yield stable salts with dilute aqueous alkali, while those possessing phenolic properties (thiophenols) dissolve in dilute alkali. Certain thiophenols are alkali-insoluble for the same reason that certain high-molecular-weight phenols are alkali-insoluble.

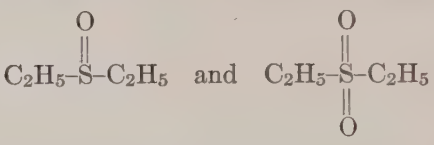
The most important reactions for compounds which may be considered as derivatives of hydrogen sulfide are the oxidation reactions. The usual reagent is either nitric acid or permanganate. For the oxidation of the sulfides to sulfoxides and sulfones, 30 per cent H_2O_2 in acetic acid as a solvent is a convenient and rapidly acting reagent. The thiols may be oxidized readily to the disulfides by any one of several reagents, such as NaOI, H_2O_2, and occasionally by the oxygen of the air.

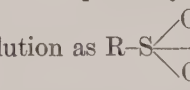


Problem 40*a*.—Write the structural formula for the compound known in chemical warfare as "mustard gas." Knowing that the corresponding sulfoxide is practically non-toxic, how would you attempt to prevent mustard

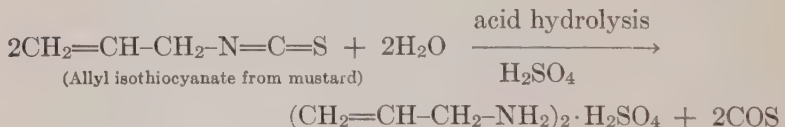
gas burns in recently exposed tissues? J. Am. Chem. Soc. **42**, 1208, 1230, (1920).

The low molecular weight sulfoxides and sulfones like



are, as might be expected from their structure, slightly soluble in water. The members possessing higher molecular weights, however, are only sparingly soluble. The greater solubility of the sulfoxides is due probably to a reaction with water and their presence in solution as  .

The isothiocyanates are of some importance since a few members are found in natural products. They are broken down by acid hydrolysis, as was noted also among the oxygen analogues, the isocyanates, to produce primary amines.

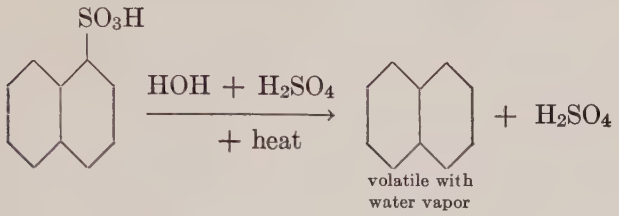


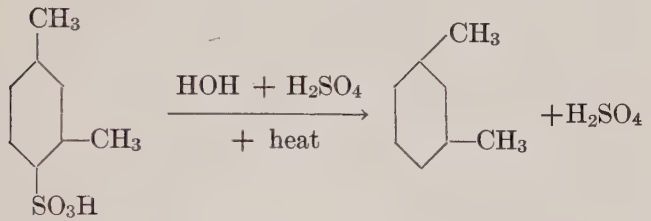
(Allyl isothiocyanate from mustard)

The most common sulfur compounds met in organic analysis are the sulfonic acids. The aromatic members are the most important since they are easily prepared and possess important technical uses.

In contrast to the sulfinic and carboxylic acids, the sulfonic acids are very highly ionized. As might be expected from their structure, they are fairly soluble in water and the lower members are therefore isolated usually in the form of salts. Many sulfonic acids may be hydrolyzed by heating with 25 per cent to 50 per cent sulfuric acid to yield the corresponding hydrocarbons or derivatives. The ease of hydrolysis differs with different members, and it appears that those compounds which are sulfonated most readily yield sulfonic acids which hydrolyze the most easily. Benzene sulfonic acid does not yield benzene except under special

conditions of hydrolysis. Toluene sulfonic acids hydrolyze with less difficulty, and the *o*– and *m*–xylene sulfonic acids, fairly readily.





The sulfonic acid group in phenols and amines may often be displaced by halogen in connection with the usual bromine-water test.

Another important technical reaction of the sulfonic acids is hydrolysis by fusion with caustic alkalis. In qualitative work, this is of minor importance.

Probelm 41.—Write the equations for the following reactions:

(*a*) Fusion of sodium benzene sulfonate with caustic alkali,
(*b*) Distillation of sodium benzoate with soda lime,
(*c*) Heating of anthraquinone-β-sulfonic acid with ammonia under pressure,
(*d*) Fusion of saccharin with caustic alkali.

As was the case with the carboxylic acids, the sulfonic acids, also, may be converted into acyl chlorides and identified as such or in the form of the amides. Since sulfonic acids and their salts usually crystallize with water of crystallization, it is important that they be dried for some time at 100° before subjecting them to the treatment with phosphorus pentachloride. The presence of other groups (such as OH, NH_2, etc.), which also react with PCl_5, will be expected to interfere with the preparation of the acyl chlorides.

Compounds Containing Special Elements.—Many metals are met in organic analysis in connection with the examination of salts. This part of the subject will require no special treatment, however, since the general method of attack consists in identifying the organic compound after it has been liberated from its salt.

The organic basic compounds are often met, of course, in the form of their salts with inorganic as well as with organic acids. Occasionally an organic compound is found combined with inorganic material as a double salt. Among the organo-metallic compounds, derivatives of magnesium, zinc, mercury, etc., are valuable laboratory reagents, although they are infrequently met in connection with organic analysis.

In the pharmaceutical field, organic arsenic, mercury, antimony, and phosphorus compounds are receiving increased attention, and similar examples might be given from other specialized lines of applied organic chemistry. An attempt to treat such specialized lines is inadvisable here.

CHAPTER V

COMPOUNDS WITH UNLIKE SUBSTITUENTS

The majority of the derivatives of the hydrocarbons (saturated and unsaturated) contain more than one substituent, and among these poly-substituted derivatives a considerable number contain *unlike* substituents. Among the commoner organic compounds this distribution is more equable, however; thus in the Tables in Part C, we find listed the constants for about two thousand fairly common organic compounds. This number is divided approximately as follows:

I. One substituent, 30 per cent,
II. Two or more like substituents, 10 per cent,
III. Two or more unlike substituents, 60 per cent.

Important classes of compounds which fall in the third subdivision are:

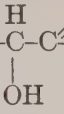
(*a*) Carbohydrates and their derivatives,
(*b*) Amino acids and their derivatives,
(*c*) Ureides, and
(*d*) Dyes.

In addition to these specialized types, each solubility group will contain other classes of compounds with unlike substituents and a part of the present chapter will deal with the possible effect of such compounds upon the simplified classification and method of analysis outlined in Chapter I. No pretense is made to treat the above specialized types except in a general elementary manner; more advanced texts are already available, dealing with analytical work in these respective fields.

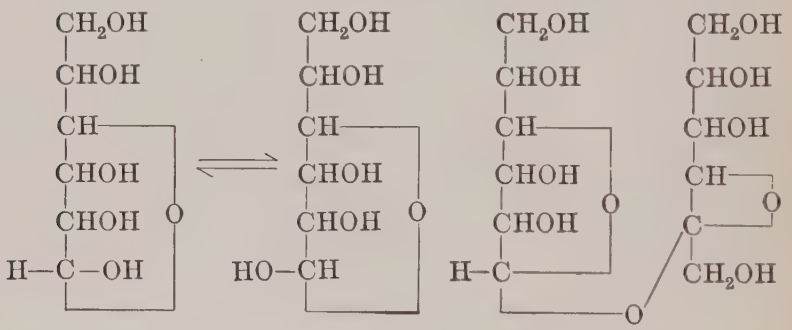
A systematic procedure of analysis might be expected to lead to narrowness on the part of the student; this is too often the case in inorganic "ion" analysis. Fortunately, organic analysis cannot be narrowed down to an analytical procedure which is inde-

pendent of a thorough knowledge of organic chemistry and of the ability to use that knowledge; the mixed classes of compounds, particularly, will prevent such an occurrence. The present chapter gives only a glimpse into the field; a region in which each organic chemist must develop by practical experience in the specialized line in which he is working.

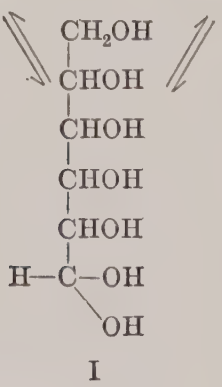
CARBOHYDRATES

The carbohydrates are compounds containing carbon, hydrogen, and oxygen, usually of the composition $C_n(H_2O)_{n \text{ or } n-1}$, which contain the sugar or " ose " group either free or in combination. The " ose " group is represented as  or a structure in equilibrium with this form.

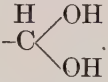
Formula I represents an aldohexose with the free sugar group; Formula II represents a disaccharose of the sucrose type with the sugar groups in combination.



II



I

The structures in (I) represent what is commonly known as the lactone formulas for a sugar; thus, *d*-glucose is known in two forms, alpha and beta *d*-glucose. Either isomer in solution is gradually converted into an equilibrium mixture which is represented by (I). This rearrangement, known as a muta-rotation, is hastened by the addition of a trace of alkali, a fact which is of importance in connection with the determination of the specific rotation of any sugar possessing the free " ose " group. The individual shown in II does not muta-rotate. The aldo sugars, although possessing a potential aldehyde group do not give the fuchsin-aldehyde test. An exception is noted also in the case of chloral hydrate, which compound possesses its aldehyde group in combination with water to produce the structure,  .

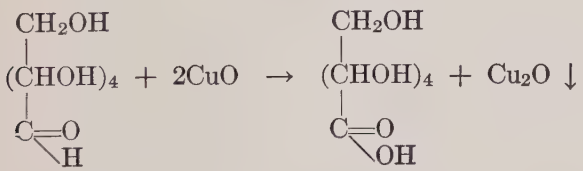
The presence or absence of the free sugar group enables a classification of compounds into (*a*) reducing sugars, and (*b*) non-reducing sugars.

The reducing sugars react readily upon heating with Fehling's Solution to give a precipitate of cuprous oxide; the second class gives no reaction with this reagent. The non-reducing sugars, however, may be hydrolyzed with varying degrees of ease to mono-saccharoses which react in the normal manner with the Fehling reagent.

Problem 42.—Explain why a disaccharose, like maltose or lactose, $C_{12}H_{22}O_{11}$, will react with Fehling's Solution.

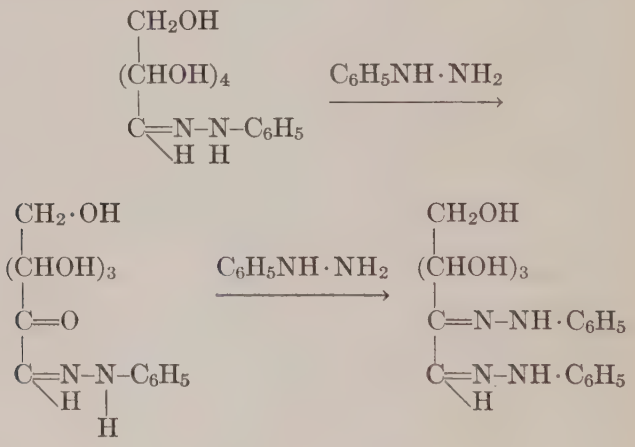
Problem 43.—The formula $C_6H_{12}O_6$ represents (*a*) how many aldohexoses, (*b*) how many ketohexoses?

Fehling's Solution may be represented as equivalent to a solution of cupric oxide and the reaction may be written as follows:

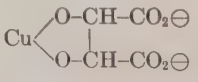


The reaction is actually somewhat more complex, not only in respect to the reagent[1] but also in respect to the products formed from the sugars, since the secondary alcohol groups in the sugar acid represented above are also susceptible to oxidation. Nevertheless, the method is available even for quantitative estimation provided that the procedure is carried out in a specified empirical manner.

A more nearly typical reaction of the sugar group is that with phenylhydrazine, resulting in the formation of an osazone. The first step is exactly analogous with the usual aldehyde and ketone reactions. Upon continued heating with phenylhydrazine solution, the alpha –CHOH group is oxidized by a molecule of phenylhydrazine to produce a carbonyl group, which then reacts again with phenylhydrazine to form a double hydrazone, known as an *osazone*.



[1] The copper in Fehling's Solution is held in combination by the tartaric acid in a form which prevents the precipitation of cupric hydroxide. Upon electrolysis of such a solution, the copper travels with the negative ion to the cathode. This complex ion is often represented as,



Reaction with Fehling's Solution is not typical of the sugar group; many other substances, both organic and inorganic, may reduce Fehling's Solution.

The various sugars differ in ease of reaction with phenylhydrazine, and consequently the " time test of osazone formation " (page 144), is of value in giving information concerning a given unknown in this group. The crystalline structure and to a minor extent the melting-points of the osazones are also of aid in identification work. Easily hydrolyzable non-reducing sugars, like sucrose, may yield osazones because of the fact that hydrolysis gradually takes place under the conditions chosen for the experiment. Such sugars naturally require a greater time for osazone formation.

Problem 44.—Explain why glucose, mannose, fructose, and sucrose give identical products in the osazone reaction.

The specific rotation is a particularly valuable constant for sugars as well as for many of their derivatives. This is of special importance for the reason that the usual melting-point test applied to poly-hydroxy compounds is somewhat dependent upon the rate of heating, and additional physical constants are therefore desirable.

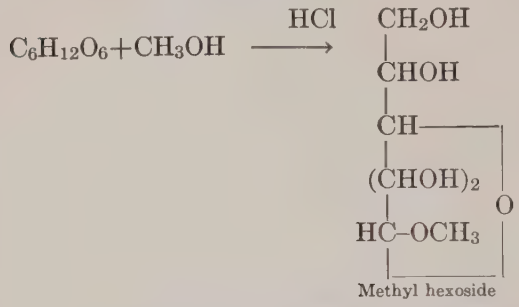
In a few instances, sugars may be isolated in the form of the simple hydrazones, but in general these derivatives are too soluble in water. By choosing hydrazines of higher molecular weight, benzyl phenylhydrazine, β-naphthylhydrazine, etc., hydrazones may be more readily isolated. Aldoses may be differentiated from ketoses by the use of asymmetrical hydrazines like $C_6H_5–\overset{\displaystyle CH_3}{\underset{|}{N}}–NH_2$. Ketoses yield the typical osazones, whereas aldo-sugars form only the colorless hydrazones.[1]

Problem 45.—According to the solubility rules in Chapter II, would you expect a hexose hydrazone to be more soluble than the corresponding osazone? Would you expect lactosazone to be more or less soluble than glucosazone?

In addition to the reactions already discussed, the sugars possess other typical reactions of the carbonyl, hydroxyl, and ether (acetal) linkages, together with a number of more specific reactions. Only a few of these will be mentioned for the reason that many of them are of synthetical rather than of analytical value.

[1] Weyl, Part I, pp. 471–2 (1911).

In connection with other aldehydes, the aldo-sugars may form acetal-like compounds when heated with anhydrous alcohol in the presence of a trace of HCl.



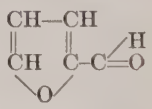
Methyl hexoside

This acetal linkage is present in the poly-saccharoses and consequently these compounds may readily be hydrolyzed to yield mixtures of mono-saccharoses. When sucrose is thus hydrolyzed, the process is called inversion. Why?

$$\text{Sucrose} + H_2O \xrightarrow{\text{dil. HCl}} \text{Glucose} + \text{Fructose}$$

The hydroxyl groups of carbohydrates may be acetylated by heating with acetic anhydride in the presence of dehydrating agents such as fused sodium acetate or zinc chloride. Aldo- and keto-hexoses form penta-acetyl derivatives, whereas disaccharoses like sucrose, maltose, and lactose form octa-acetyl derivatives.

Pentoses, pentosides, as well as polyoses which yield pentoses upon hydrolysis, readily form furfural,



when distilled with dilute mineral acids. This heterocyclic aldehyde may be identified as the phenylhydrazone; it may be detected qualitatively due to the formation of an intensely colored red dye with aniline acetate solution. In quantitative work, pentoses are determined by converting them into furfural and estimating the latter either with phloroglucinol [1] or with thiobarbituric acid.[1]

The pentoses are not fermented by yeast enzymes, whereas most hexoses are readily attacked. Alcoholic fermentation has been observed among trioses, hexoses, and nonoses, which is in agreement with the equation:

$$(C_3H_6O_3)_x \xrightarrow{\text{enzyme}} xC_2H_5OH + xCO_2.$$

[1] J. Am. Chem. Soc. **38**, 2156 (1916).

The formula $(C_6H_{10}O_5)_x$ represents the complex carbohydrates such as dextrins, starches, and cellulose. A general test for these classes as well as the simple carbohydrates already discussed is the Molisch color test, which is based upon the colors produced when a trace of carbohydrate material is treated with sulfuric acid in the presence of α-naphthol.[1]

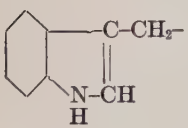
Starch occurs in the form of granules which differ considerably in appearance according to the plant from which it is obtained. Microscopic examination is therefore of considerable aid in learning the source (potato, rice, corn, rye, etc.). In cold water, the granules are insoluble but they swell and burst upon heating and yield colloidal starch solutions. Starches give a typical blue color even with traces of iodine, but are readily hydrolyzed by diastase to dextrins, which no longer respond to this typical test, and finally to reducing sugars. Dextrins, as well as starches and cellulose, may be hydrolyzed by means of mineral acids to yield reducing sugars.

AMINO ACIDS

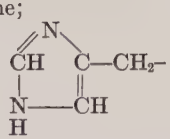
The most common aliphatic amino acids possess the formula $R{-}\underset{\displaystyle NH_2}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}{-}CO_2H$.[2] They are derived not only from mono, but also from dicarboxylic acids, and among the members from natural products a few are known to possess an amino group on a carbon atom other than the α-carbon. Lysine, α, ϵ-diaminocaproic acid, $NH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}\underset{\displaystyle NH_2}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}{-}CO_2H$, is probably the best known example of the latter type.

[1] Mulliken, Vol. I, p. 26.

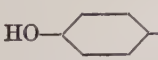
[2] The radical R– may be H as in glycocoll; alkyl as in α-alanine, leucine, etc.; $-CH_2OH$ as in serine;



as in tryptophane,



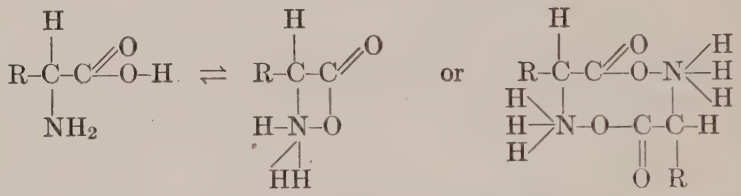
as in histidine;



as in tyrosine;

$-CH_2{-}S{-}S{-}CH_2-$ as in cystine, etc.

Amino acids give deep red colorations with ferric chloride and, as would be expected from their relation to ammonia, give a deep blue color with solutions of cupric salts. The simple α-amino acids are practically neutral in reaction; they may be considered as inner salts.



As might be expected from these structures, the lower members, like glycocoll and alanine, are very soluble in water but insoluble in ether. (Solubility Group II.) Members of higher molecular weight fall in Groups III and IV. In general, they do not possess definite melting-points.

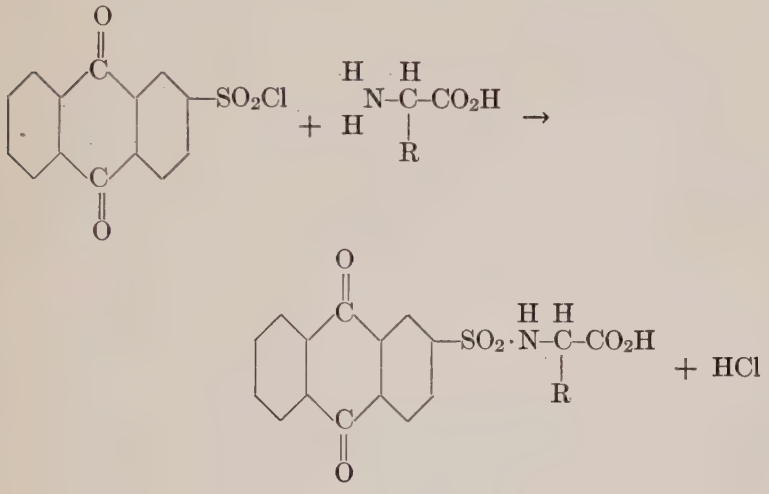
With nitrous acid, the α-amino acids react very readily to yield nitrogen gas and α-hydroxy acids which usually cannot be isolated with ease. An excellent volumetric method for the estimation of amino acids is based upon this reaction.[1]

In the presence of an excess of concentrated hydrochloric acid and the calculated amount of $NaNO_2$, the chloro derivatives of the aliphatic acids are obtained, often in good yield.[2] The most valuable reaction of amino acids for use in the qualitative laboratory is the preparation of acyl derivatives. Valuable reagents[3] for this purpose are benzoyl chloride, benzene sulfonyl chloride, β-naphthalene sulfonyl chloride, and β-anthraquinone sulfonyl chloride, all of which may be used with aqueous solutions of amino acids, since these acyl chlorides are only slowly decomposed by water. When benzoyl chloride is used, the product obtained may be contaminated with a small amount of benzoic acid, which may usually be removed because of its greater solubility in ether. The benzoyl derivatives of the amino acids are often rather sparingly soluble in ether as is true of many amides.

The acyl chlorides derived from sulfonic acids possess the advantage that the organic acid formed as a by-product is usually

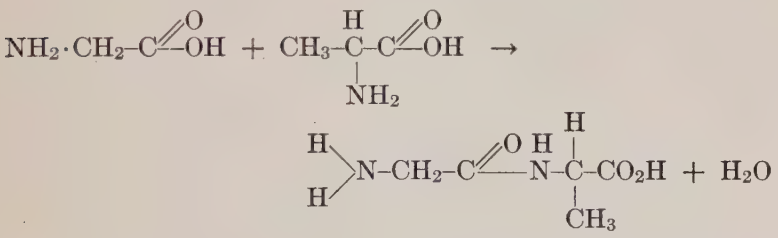
[1] Van Slyke, J. Biol. Chem. **12**, 275 (1912); **16**, 121–125 (1913).
[2] Z. Physiol. Chem. **31**, 119 (1900).
[3] Ber. **35**, 3779 (1902); Ber. **33**, 3526 (1900).

soluble in water. Benzene sulfonyl chloride is the most common reagent of this type used in qualitative work. When the corresponding sulfonyl derivatives are too soluble in water, a high molecular weight acyl halide, anthraquinone sulfonyl chloride, may be used.



Peptides

The polypeptides are compounds in which the carboxyl group of one amino acid has reacted with the amino group of a second amino acid to produce an amide structure.



Glycyl alanine, the compound formed in the hypothetical reaction above, is called a dipeptide. Continued amide formation with additional amino acids would lead to the formation of tri- and tetra-peptides, etc. These polypeptides possess in addition to the reaction of the amino acids the hydrolytic reactions due to

the presence of the amide structure. They are products which have not only been prepared synthetically but which have also been isolated as intermediate products in the hydrolysis of proteins.

Since the sulfone amides are hydrolyzed less readily than the amides of carboxylic acids, we have in benzene sulfonyl chloride a reagent not only for the isolation and identification of some of these substances but also a means for determining the structure of a given product.[1] For example, glycocoll and alanine may be combined to yield two different products. After reaction with benzene sulfonyl chloride and hydrolysis of the resultant products, we shall obtain in one instance a glycocoll residue united to the sulfonyl radical, whereas in the second instance alanine is obtained in the form of its sulfonyl derivative.

Proteins

The proteins form the bulk of the nitrogenous contents of plant and animal cells. They contain chiefly carbon, hydrogen, oxygen, and nitrogen, the percentage of the latter varying between narrow limits (15 to 17.5 per cent). Small amounts of sulphur are often present, and occasionally also phosphorus. These compounds are of very high molecular weight, usually non-crystallizable, and in solution are present in the colloidal state. They may be hydrolyzed to yield amino acids and other products whereas some individuals among the conjugated proteins yield also purines and pyrimidine bases, phosphoric acid, and carbohydrates.

Soluble proteins may usually be precipitated by a variety of reagents, and many of them may be coagulated by heating. Some of the common salts, like ammonium sulfate, sodium sulfate, sodium chloride, etc., serve for "salting out" of many of these members in the unaltered condition, while certain acids (picric, tannic, phosphotungstic, phosphomolybdic, etc.) serve for their removal as insoluble salts.

In addition to the precipitation reagents, a large variety of color-tests is in use for the detection of proteins. (*A*) In Millon's Reaction, the material is treated with nitric acid, in which a small

[1] Ber. **40**, 3548 (1907).

amount of mercury has been dissolved. Upon heating, the protein assumes a red color. (*B*) Under the formidable name of Xanthoproteic Reaction, so-called because of the production of a yellow color, we meet a common test for the phenolic group. When a drop of nitric acid is placed upon the skin, a yellow stain develops which, when washed and treated with alkali, turns to a deep orange. (*C*) The Biuret Test is based upon the colors produced (pink to bluish) when the protein, in strongly alkaline solution, is treated with a very dilute copper sulfate solution. When present in urine, albumin may be detected by the nitric acid ring test either by the formation of a white zone of precipitated albumin or by the heat coagulation test followed by the addition of a drop of acetic acid.

The proteins are usually classified into three groups:

I. **The Simple Proteins** yield only alpha-amino acids or their derivatives upon hydrolysis: this group comprises albumins, globulins, glutelins, prolamines, albuminoids, histones, and protamines.

II. **Conjugated Proteins** contain the protein molecule united with some other molecule in some manner other than as a salt, Nucleoproteins, glycoproteins, phosphoproteins, hemoglobins, etc., are typical members.

III. **Derived Proteins** are formed from the first two groups. due to hydrolytic changes. The group comprises proteans, metaproteins, coagulated proteins, proteoses, peptones, and peptides.

Further classification of the simple proteins is of interest to the student of organic analysis because of the application of solubility behavior for the classification of this group of complex natural products, viz.:

Simple Proteins:

1. Albumins. Soluble in water but coagulated by heat.
2. Globulins. Insoluble in water but soluble in neutral salt solution.
3. Glutelins. Insoluble in neutral solvents but soluble in dilute acids and alkali.
4. Prolamines. Insoluble in water but soluble in 70 per cent alcohol.
5. Albuminoids. Insoluble in all neutral solvents.

6. Histones. Soluble in water but precipitated by ammonia.
7. Protamines. Soluble in water but not coagulated by heat.

For analytical work in this special field, the advanced texts referred to at the end of the chapter should be consulted.

AROMATIC AMINO ACIDS

Many amino acids derived from aromatic acids differ appreciably from the aliphatic type because of the feeble basicity of the amine group. In general, these compounds possess definite melting-points and appreciable solubility in ether. Since the amino group is very feebly basic (page 20), these acids may usually be titrated in the presence of phenolphthalein and a fairly accurate neutral equivalent obtained. A specific example will be treated below in the general discussion of compounds containing several reactive groups.

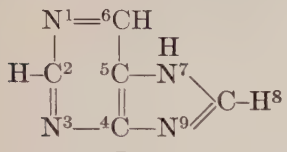
In addition to derivatives of aromatic carboxylic acids, a large number of amino derivatives of aromatic sulfonic acids is known. Many of these compounds are of importance as dye intermediates. Due to the presence of the sulfonic acid group, they are no longer ether-soluble. Many of the members are of fairly high molecular weight and hence of limited solubility in water. Acids of this type, together with phenolic sulfonic acids and compounds, which possess both the phenolic and the amino groups, are met in commerce under names such as the following: H acid, F acid, Gamma acid, G salt, R salt, Broenner's acid, Cleves' acid, Neville and Winther's acid, etc.

A few of the commoner members are known by names which are more suggestive of their structure, such as sulfanilic acid, metanilic acid, naphthionic acid, etc.

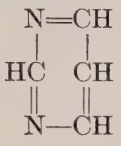
THE UREIDES

Urea, $NH_2{-}\overset{\overset{O}{\|}}{C}{-}NH_2$, is the amide of carbonic acid. It may be condensed with various acids to produce substituted amides which are known as ureides. In addition to these simple compounds,

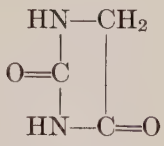
several groups of cyclic ureides are of importance, particularly the purines, pyrimidines, and hydantoins.



Purine



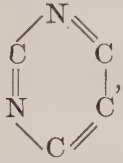
Pyrimidine



Hydantoin

Although the mother substances, purine and pyrimidine, are not themselves important, many of their derivatives occur in natural products. Only a few can be mentioned here.

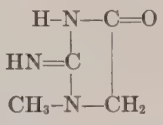
2, 6-Dihydroxy purine.....Xanthine
2, 6, 8-Trihydroxy purine.....Uric Acid
2, 6-Dihydroxy-3, 7-dimethyl purine.....Theobromine
2, 6-Dihydroxy-1, 3-dimethyl purine.....Theophylline
2, 6-Dihydroxy-1, 3, 7-trimethyl purine.....Caffeine
6-Hydroxy-2-amino purine.....Guanine

These compounds exhibit typical reactions which may be predicted according to their structures; some of them, however, possess unusual stability towards hydrolysis when compared with the simple urea derivatives. Such variations in stability are no doubt associated with the stabilities of the heterocyclic structures. Thus, the purines or pyrimidines may be considered as possessing a nucleus,  , which in some respects is comparable with the benzene nucleus. Hydantoin, on the other hand, when heated with dilute alkali, readily hydrolyzes to hydantoic acid and then into ammonia, carbon dioxide, and glycocoll. It is feebly acidic, as might be expected from the imide structure, and appreciably soluble in water, as might also be predicted from its structure, and the melting-point of 216°.

Uric acid is a fairly strong acid; it dissolves readily in dilute alkali, and is precipitated from alkaline solution in the form of a sparingly soluble acid-salt by means of carbon dioxide. It is fairly resistant towards hydrolysis. Caffeine, on the other hand,

possesses no acidic hydrogen but is feebly basic, as might be expected from its structure. Heating with alkali results in hydrolytic action.

Problem 46.—Predict the products formed when creatinin



is subjected to hydrolysis by boiling in alkaline solution.

An important test often applied to the purine derivatives in order to differentiate them from other amides is the murexide reaction. A small quantity of the compound (1/100 g.) is moistened with a few drops of 1/1 HCl. A minute crystal of $KClO_3$ is added and the mixture evaporated on a crucible cover upon the steam-bath. A pinkish or yellowish color is usually apparent at this stage, and this color deepens upon gentle warming of the residue over a free flame. After cooling, the reaction product is moistened with a drop of ammonia water, which results in the production of a purplish color.[1]

Nitrogen determinations by the Kjeldahl method are important in connection with the identification of compounds of this type.

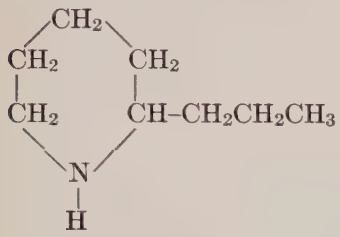
ALKALOIDS

The alkaloids are basic compounds possessing at least one heterocyclic nitrogen atom. These compounds, many of which exhibit powerful physiological action, occur generally in certain plants. The term *alkaloid* is often applied, however, in a broader sense so as to include compounds of the purine and pyrimidine types which occur in the animal body as well as in plants. Many members of the latter type are not basic but, like uric acid, are really acidic compounds. A still broader classification might include many other nitrogenous compounds, natural as well as synthetic (adrenalin, novocaine, etc.), which do not contain heterocyclic nitrogen atoms but which exhibit physiological behavior suggestive of the vegetable alkaloids.

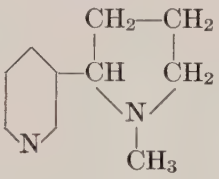
In general, the alkaloids possess a variety of unlike substituents although certain members are relatively simple and may be

[1] Ber. **30**, 2236 (Suppl.); Mulliken, **2**, 31.

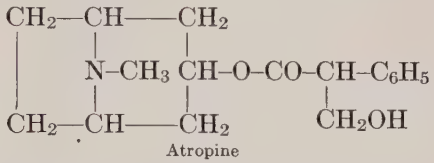
considered as substituted hydrocarbons possessing only one or two reactive groups. For example, coniine behaves exactly like other secondary amines, nicotine is relatively more complex, whereas in atropine we have an example of the presence of a variety of unlike groups in the same molecule.



Coniine



Nicotine



Atropine

Problem 47.—Point out the asymmetric carbon atoms in the formulas for coniine, nicotine, and atropine. Are the natural products optically active?

What is formed when coniine is subjected to exhaustive methylation? (Ref. Stewart, Recent Advances in Organic Chemistry,1918, pp. 125–6.)

Such compounds, even when a considerable number of unlike substituents is present, will occasion no special difficulty. The well-known members, including a few the structures of which are not known with certainty, are included in the tables for common organic compounds given in Part C.

The reason for a specialized treatment of alkaloids in most schemes of analysis is not due to any unusual variation from the reactions predicted for the substituents present but because of the powerful physiological action of many individual members. Because of the latter reason, the compounds are often met in extremely minute quantities, as for instance, in connection with the toxicological examination of animal tissues. In such instances, the methods of microanalysis are frequently of value.

Since alkaloids often occur in minute quantities, classification based upon color reactions with various alkaloidal reagents is generally used. The individual members may sometimes be detected by means of their typical physiological behaviors.

For work in this field, the larger texts must be consulted, particularly the special treatises upon the subject. References are given at the end of this chapter.

ORGANIC DYES

The common classes of organic dyes are the following:

(1) Azo Dyes: { Monoazo, Di-azo, Tri-azo, etc.

(2) Triphenylmethane Dyes: { Malachite green series, Rosaniline series, Auramines or Rosolic acid series, Phthaleins, Rhodamines, and Eosines,

(3) Diphenylmethane Dyes: { Pyronines, Acridines, Auramines,

(4) Vat Dyes: { Indigo type, Anthraquinone type (Indanthrenes),

(5) Anthracene dyes of the alizarin type,

(6) Nitro and Nitroso dyes,

(7) Sulfur dyes (Sulfide colors, Thiazines, etc.),

(8) Diphenylamine Dyes: { Indamine, Indophenols, Thiazine, Oxazine, Safranines.

Problem 48.—As an exercise, the student should write the formulas for various dyes found in the above classes. He may limit himself to the specific classes which are studied in his general course in organic chemistry.

Problem 49.—Give a list of (*a*) the common chromophore groups, (*b*) the common auxochrome groups.

The examination of organic dyes, particularly because of the large number of individual compounds and mixtures ordinarily met in technical products, is work for the specialist. Attempts have been made toward the systematic grouping of dyes based upon chemical reactions. Thus the scheme of Rota[1] is based

[1] Chem. Zeit. 1898, 437.

upon the behavior of dyes towards various reducing and oxidizing agents. Rota has suggested the following classification:

TABLE XX

UNKNOWN IN 1 : 10,000 SOLUTION (WATER OR ALCOHOL)

Treat with dilute HCl and $SnCl_2$

Reduction to colorless solution. Neutralize and add $FeCl_3$.		No reduction by $SnCl_2$. To original solution add 20% KOH and warm	
Color not restored	Color restored	Decolorization or precipitate	No precipitation and color deepens
Class I	Class II	Class III	Class IV

Further discussion of this scheme of classification and the methods used for subdivision of the four main classes is not justifiable in the space available here.

Effective work in connection with the identification of dyes usually requires also actual dyeing experiments. A particularly valuable physical property which is utilized in connection with the identification of dyes is the absorption spectrum of dye-solutions.

A more recent and far more extensive treatment for the identification of dyes has been developed by Mulliken, Identification of Pure Organic Compounds, Vol. III. About fifteen hundred dyes are classified in this extended treatise. The method of attack is as follows:

Preliminary Tests:

(1) Homogeneity test (*a*) water, (*b*) sulfuric acid, (*c*) fractional dyeing, (*d*) capillary absorption, (*e*) spectroscopy,
(2) General appearance and color,
(3) Solubilities in water, alcohol, sulfuric acid,
(4) Tests for sulfur dyes,
(5) Direct dyeing of wool and cotton,
(6) Dyeing with hydrosulfite vat,
(7) Dyeing with sodium sulfide vat.

Generic or Divisional Tests:
- (8) Discharge of direct wool dyeings by sodium formaldehyde sulfoxylate,
- (9) Restoration of color by air,
- (10) Restoration of color by potassium persulfate,
- (11) Color discharges and returns on vat-dyed cotton.

Coordination Tests:
- Action of H_2SO_4 on textile dyeings,
- Action of NaOH on textile dyeings,
- Action of nitrous acid on wool dyeings.

Special Tests:
- Precipitation tests—H_2SO_4, NaOH, sulfates of Ca, Cr, Cu, and tannin,
- Dyeing on mordanted wool,
- Diazotization and development with β-naphthol,
- Reduction products of azo dyes,
- Absorption spectra.

Verification test and use of color standard.

The scheme proposed by Mulliken naturally finds more or less criticism from the specialists in the dye industry. No doubt much valuable information has been developed in the research laboratories of the dye works but only a limited amount of such data becomes public property. The technical worker who is most prolific in his criticism is usually the one who is most secretive with his own results.

The particular dyes which are permitted by the U. S. Government in foods and beverages have been limited to ten.[1] These have been selected because they are relatively harmless; they may be readily manufactured in the pure condition; and they may be readily identified.[2] These colors, which are also met in the form of mixtures, may be classified as follows:

Red shades
- 107. Amaranth,
- 56. Ponceau 3R,
- 517. Erythrosine.

[1] U. S. Dept. of Agriculture, Decisions Governing Colors in Food.
[2] Leach, Food Inspection and Analysis.

Orange shade
85. Orange I.
Yellow shades
4. Naphthol yellow S,
94. Tartrazine,
Yellow A.B. (Benzenazo-β-naphthylamine) m. 103°,
Yellow O.B. (Ortho-toluenazo-β-naphthylamine) m. 126°.
Green shade
435. Light green S.F. yellowish.
Blue shade
692. Indigo disulfoacid.

The numbers preceding the names refer to the numbers of the colors as listed in A. G. Green's edition of the Schultz-Julius Systematic Survey of the Organic Coloring Matters, published in 1904.

An important reaction of the azo dyes consists in their reduction to the corresponding amino compounds. An important reagent for this purpose is stannous chloride in hydrochloric acid solution. In this reduction, compounds are broken between the two nitrogens of the azo group and from the resultant simpler compounds, the structure of the original dye may often be deduced.

Problem 50.—An azo dye upon reduction yielded benzidine, *p*-amino-dimethylaniline and 1-amino-2-hydroxynaphthalene on reduction. What is the structure of the dye and what products serve as intermediates for its manufacture?

Problem 51.—What are the indanthrene dyes? (Ref. Stewart, Recent Advances of Organic Chemistry, 1918, p. 6.)

EFFECT OF POLY-SUBSTITUTION

In the discussion of chemical reactions, we have for the most part considered simple *type* compounds. Several examples have been met which demonstrate that the simultaneous presence of several substituents may lead to a modification of the usual reactions. The present section will summarize some of the examples already discussed and will offer additional illustrations from the standpoint of possible effect upon the proposed scheme of analysis.

In Chapter II, we noted the fact that the $-NH_2$ group in an organic molecule may be basic, neutral, or even acidic; the particular behavior towards ionization depends upon the group joined

to the amine nitrogen. Groups which when substituted into the molecule lower the basicity of a base or increase the acidity of an acid are often spoken of as negative groups. It is not essential that the negative group be directly joined to the amine group. Aniline is a weak base but substitution by the nitro group decreases the basicity still farther. Meta and *p*-nitraniline are only feebly basic but there is no doubt but that they fall in solubility Group III. A nitro group in the ortho position, however, exerts a still greater effect and we find *o*-nitraniline and 2, 4-dinitraniline to be almost insoluble in dilute acids. Halogens exert an effect similar to, but less powerful than, the nitro group. The substitution of three halogen atoms into aniline yields a compound that is only feebly basic.

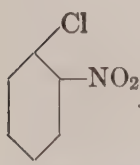
The union between carbon and nitrogen is fairly stable towards hydrolysis; negative substitution, however. leads to instability.

$$\left.\begin{matrix} R{-}NH_2 \\ Ar{-}NH_2 \end{matrix}\right\} + \text{alkali} \xrightarrow{\text{heat}} \text{No reaction.}$$

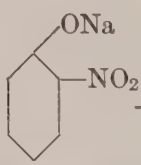
$$C_6H_4\begin{matrix} NH_2(^1) \\ NO_2(_{2\text{ or }4}) \end{matrix} + \text{alkali} \xrightarrow{\text{heat}} C_6H_4\begin{matrix} OH(^1) \\ NO_2(_{2\text{ or }4}) \end{matrix} + NH_3$$

Nitro groups exert a similar effect upon the labilization of halogen, the effect being greatest in the ortho position.

$$+ \text{alkali} + \text{heat} \xrightarrow{\text{alc. sol'n}} \text{No reaction unless at very high temperature under pressure.}$$



$$+ 2NaOH + \text{heat} \rightarrow$$

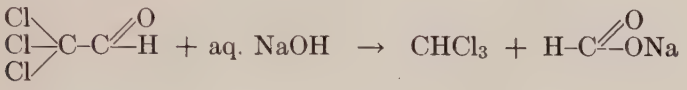


$$+ NaCl + H_2O$$

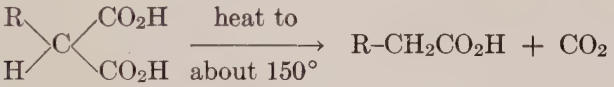
The union between carbon and carbon is generally very stable and is ruptured only by high-temperature reactions. We have already observed, page 43, however, that in the structure

$$-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-$$

we can readily disrupt the union between carbon and carbon. This is true also when a carbon atom adjacent to the carbonyl is heavily substituted by halogen.



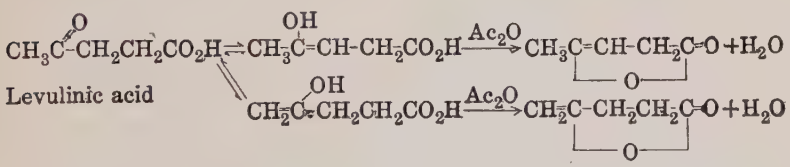
Carboxylic acids do not readily lose carbon dioxide except at high temperatures or when fused with caustic. When two carboxyl groups are joined to the same carbon atom, one molecule of carbon dioxide is readily lost:



Dicarboxylic acids with the two carboxyl groups in the α, β or α, γ positions readily undergo anhydride formation when heated either alone but preferably with dehydrating agents. Such reactions are expected when the substituent groups are in positions favoring formations of 5- or 6-atom cyclic structures.

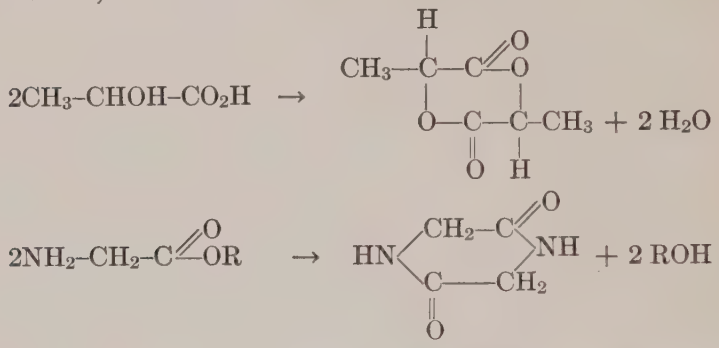
Problem 52.—Illustrate the formation of succinic, maleic, and phthalic anhydrides. What is produced when calcium glutarate is subjected to a high temperature?

A reaction analogous with that of cyclic-anhydride-formation is the formation of lactones from γ-hydroxy acids and from γ-halogen acids. (Cf. page 39.) A related reaction is the dehydration of acids possessing a carbonyl group in the gamma position.

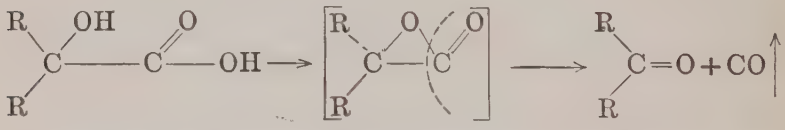


Problem 53.—According to the theory of geometrical isomerism, one of the above lactones may exist in two forms. Explain this case.

α-Hydroxy acids and α-amino acids may also form anhydrides but in such instances two molecules of the substituted acid (or derivative) are concerned.

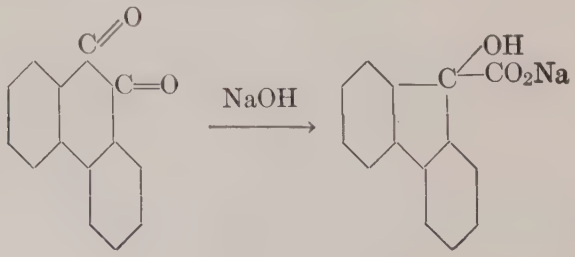


α-Hydroxy acids are readily decomposed when heated with sulfuric acid, to yield carbon-monoxide and a carbonyl derivative. The formation of an unstable α-lactone structure, by dehydration reaction, is probably responsible for this behavior. By analogous reaction, oxalic acid is expected to furnish equal volumes of carbon monoxide and carbon dioxide.



Problem 54.—β-Lactones are usually unstable and break down to yield carbon dioxide and an ethylene derivative. Write the equation for such a reaction.

The hydrolysis reaction of 1, 3 diketones have already been considered. The 1, 2 diketones in the aromatic series when heated in alkaline solution show an interesting reaction—the rearrangement to hydroxy acids.



Problem 55.—Write the equation for the reaction of 1, 2 diphenyl-ethanedione-1,2 with concentrated alkali. What is the name for this rearrangement?

Problem 56.—What is the pinacone-pinacolin rearrangement?

Although this treatment of the behavior of poly-substituted compounds is necessarily limited, sufficient material has been presented to show that these so-called complications are not such in reality, but instead are of considerable aid in analytical work; even the present superficial treatment of the subject may have served to suggest that these apparent exceptions are fairly general among themselves and therefore may be utilized for further systematization of the work.

BEHAVIOR OF POLY-SUBSTITUTED COMPOUNDS IN CONNECTION WITH IDENTIFICATION WORK

The question concerning possible complications introduced in the scheme of analysis by the occurrence of compounds possessing two, three, or four substituents will be treated with a few examples, presenting, however, only a part of the usual laboratory data.

(*a*) The formula, $C_6H_3\begin{cases}OCH_3\\ O-C-R\\ CO_2H\end{cases}$ (with O double-bonded to C), represents an ether, an ester, and a carboxylic acid. The preliminary tests will probably detect only the acidic group and this will place the compound in Group IV, but until we have proof to the contrary we shall consider the possibility of the simultaneous presence of any number of indifferent groups. The relatively high neutral equivalent (above 200) suggests the possibility that indifferent groups are present. We may therefore test for the presence of such groups, remembering, however, that the acidic group known to be present may complicate our tests slightly. In applying a phenylhydrazine test, for example, we shall consider the possibility of precipitation of a hydrazine salt. The most common tests to which we shall subject such unknowns, in addition to tests with Br_2 water, $FeCl_3$, etc., are attempts at hydrolysis with alkali or acid. Since the unknown is soluble in dilute alkali, the alkaline solution is refluxed for a short time. Acidification precipitates an acid but melting-point and neutral equivalent show that the original substance has

undergone hydrolysis, and the change in neutral equivalent tells us the molecular weight of the group that has been eliminated. Moreover, the recovered acid in contrast to the original unknown now shows phenolic characteristics.

With these facts, together with the physical constants, we are now prepared to turn to the classified tables of Group IV (or to the larger reference books if necessary) and plan additional work for the conclusive proof of identity.

(*b*) The compound, C_6H_2(–CO_2H, –Br, –O–CH_3, –NH_2), is insoluble in water but soluble both in dilute alkali and dilute acid; we shall *later* look for the compound in both Solubility Groups III and IV. *Other indifferent groups may also be present.* Since nitrogen is present, the acidic group might prove to be acidic nitrogen, but since the compound yields a reasonable value for neutral equivalent (and a sharp end-point in titration) we provisionally assume the presence of a fairly strong acidic group like carboxyl.

Bromine is present as shown by analysis, and boiling the solution of the unknown in dilute alkali fails to remove halogen.

Because of its basic nature the compound is tested with acetic anhydride. Since the reaction product is insoluble in dilute acid, we conclude that the unknown is either a I or II amine, but the sulfonyl chloride test in this case will not differentiate between these two classes. Why not? Attempted hydrolysis by boiling in both acid and alkaline solution (why may aqueous instead of alcoholic solutions be used?) indicates the presence of a substance stable towards hydrolysis.

With this information at hand, we may now consult the tables listing compounds in Groups III and IV, and plan subsequent specific tests. A direct proof of the presence of –OCH_3 will probably be unnecessary. Kjeldahl analysis for nitrogen might have aided in the earlier stages of analysis as well as in presentation of final evidence.

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PART B

LABORATORY DIRECTIONS

CHAPTER VI

PROCEDURE FOR THE ANALYSIS OF AN INDIVIDUAL COMPOUND

Solubility reactions are made the basis for dividing organic compounds into a definite number of groups. In the case of an unknown substance, the elementary analysis, as well as the physical properties of the compound, will still further narrow down the number of possibilities. In order to decide *definitely* to which homologous series a certain compound belongs, it is necessary next to apply class reactions, i.e., homologous tests. The unknown should be subjected to those homologous tests, and only those, which are justified on the basis of the solubility reactions and the elementary analysis; it is only in this manner that qualitative organic analysis can receive a logical treatment. Finally, when the homologous series to which the unknown belongs has been located, the physical properties of the compound will locate the individual within this series. It is desirable, however, to follow the above procedure by a confirmatory test which consists in the preparation of one or more simple derivatives and a determination of the physical constants of the latter.

Chapter I should be re-read before proceeding with the identification work.

OUTLINED METHOD OF ATTACK

The suggested steps in a systematic procedure for the identification of an individual organic compound are:

1. Physical examination,
2. Determination of constants,
3. Elementary analysis,
4. Solubility tests,
5. Homologous tests,
6. Consultation of literature,
7. Preparation of derivatives.

1. Physical Examination.—Examine the unknown for homogeneity, color, odor,[1] crystalline structure, etc., after a careful purification, if the compound is not pure when obtained. Observe the behavior of the substance in the ignition test. (Exp. 1, page 132.) If the substance burns readily or leaves a carbonaceous residue, it may be considered as organic. A few common organic compounds rich in oxygen or nitrogen (urea, formic acid, etc.), do not burn readily. Test any residue after ignition for alkalinity and if appreciable in amount, thus indicating more than a trace of impurity, examine it by the usual qualitative inorganic method. Carefully record these observations but do not be misled or prejudiced in your subsequent work by preliminary observations. The color of the unknown may be due to the presence of traces of impurities, particularly of oxidation products; an apparently typical odor may prove to be due to a mere trace of an odoriferous impurity.

2. Determination of Constants.—Determine first the melting-points of solids and the boiling-points of liquids. In many instances, both constants may be determined and, if so, this is highly desirable. From the behavior of solids in the ignition test, determine whether a melting-point determination is advisable. Usually with salts it is necessary to determine the constants of the free organic compound after liberation from the salt. Certain organic liquids decompose upon distillation, and for this reason any vis-

[1] The taste of certain organic compounds is occasionally of value to the analyst but because of the obvious danger involved this test should *never* be applied at this stage of the analysis when the nature of the compound is entirely unknown.

cous-appearing liquid should be tested (how?) before attempting to distil the sample.

A specific gravity determination is especially valuable for liquid unknowns (page 118). The weighed sample should be reserved for use in a later test where a weighed amount of material may be required.

Other physical constants, such as refractive index, optical rotation, semi-quantitative solubility determinations in solvents of different types, etc., are reserved until later in the course of analysis, since their application may possibly prove unnecessary.

3. Elementary Analysis.—Analyze the unknown for carbon, nitrogen, halogens, sulfur, and metallic residue left upon ignition. (See Chapter VII for details.) A test for hydrogen is unnecessary. Tests for special elements—phosphorus, arsenic, lead, mercury, etc., are not applied as a routine procedure in this course but when such tests are necessary they will be suggested in connection with Steps 4 and 5. In applied work, the source of the material or the usual information concerning the use for the substance under examination is usually of value in suggesting the advisability of testing for special elements.

Quantitative analyses for any characteristic element is occasionally applied in connection with the final identification in Step 7. (See Chapter XI.) As a general rule, it is advisable to titrate any alkaline residue left upon ignition in order to differentiate between traces and appreciable amounts of alkalinity.

4. Solubility Tests.—Determine the solubility of the unknown in water, dilute alkali, dilute acid, ether, and cold concentrated H_2SO_4. For details and discussion see Chapters II and VIII. Finally consult the Solubility Table at the end of this text.

5. Homologous Tests.—Prepare a list of homologous series to which the compound might belong, drawing your conclusions from the solubility reactions, the elementary analysis, and the physical properties of the compound. Allow for the presence of indifferent groups (*including unsaturation*) not specifically detected in the solubility tests.

Apply homologous tests for those types (and only those) which are included in your list of possibilities. Suggestions for this work are obtained not only from the experimental work in Chapter IX, but also from Chapters III, IV, and V.

6. Consultation of Literature.—After the application of class reactions, the compound may be limited to a very small number of homologous series and often to one homologous series. At this stage, but not before, should the table of physical constants be consulted. If the unknown is not found in these tables listing several thousand of the simpler substances liable to be encountered then the larger reference books, such as Mulliken and Rosenthaler, must be consulted.

7. Preparation of Derivatives.—Apply confirmatory tests by preparing one or more characteristic derivatives (Chapter X) and determine the physical constants of these derivatives. A color reaction, although of value as an indication, cannot be accepted as a confirmatory test. Neutral equivalents, saponification equivalents, volatility constants of certain aliphatic acids, and quantitative estimation of groups, are occasionally equivalent to a derivative. Usually one typical derivative is sufficient but the amount of confirmatory work will depend upon the requirements for the differentiation between the individual compounds that are accepted as possibilities after completion of the work in the preceding six sections.

LABORATORY NOTES

Record all observations directly into your laboratory note-book and do this in the order in which tests are made as directed in the procedure above. The conclusion drawn from any observations and the process of reasoning involved should also appear in the note-book, and will be of assistance to enable the instructor to offer helfpul criticism. The most important object in a beginning course in organic analysis is not so much the correct solution of a given unknown which is the invariable result when comparatively simple unknowns are met, but the manner in which the conclusion is derived. The student is not limited to the above procedure in connection with all of his identification work in the laboratory. In fact, he is asked to apply the directions only to the first three simple unknowns, after which he is urged to study, apply, and compare the procedures for identification as given in other manuals, such as Clarke, Mulliken, and Rosenthaler.

CHAPTER VII

DETERMINATION OF PHYSICAL CONSTANTS AND ANALYSIS FOR THE ELEMENTS

The steps essential to a systematic and successful identification of an individual organic compound have been outlined briefly in the preceding chapter. The term *pure organic compound* has been intentionally avoided, since the analyst seldom meets such individuals.

The identification work in connection with this course will consist of the identification of six or eight individual compounds and subsequently some experience will be offered also in connection with the separation of mixtures. (Chapter XII.) Some of the individual compounds may, however, require purification; it will be advisable never to assume unreservedly a high degree of purity but to approach each problem in an unorthodox attitude and draw every conclusion in accordance. In this course "constant boiling-points" and "sharp melting-points" will not be taken as absolute criteria of purity; such constants justify submission of the unknown to the regular identification procedure but subsequent tests (solubility, class reactions, preparation of derivatives, etc.), will provide the necessary supplementary evidence regarding purity. An actual example taken from the laboratory will illustrate this point.

A given unknown [1] appeared to be pure since the boiling-point was fairly constant at 198°–199° while preliminary examination and solubility test gave no indication of a mixture. By means of the usual systematic tests the unknown was limited to the class of primary aromatic amines, and consultation of the tables (page 200) suggested the following individual possibilities:

[1] The sample was purchased on the market as *o*-toluidine of special purity.

B.p. 199° *o*-Toluidine Acetyl Der. m. 112° Benzoyl Der. m. 142°
200° *p*-Toluidine
m.p. 42° Acetyl Der. m. 148° Benzoyl Der. m. 158°
203° *m*-Toluidine Acetyl Der. m. 65° Benzoyl Der. m. 125°
205° *l*-Menthylamine

Since *p*-toluidine is a solid, it appeared to be excluded from the list of possibilities. However, the acetyl derivative of the unknown melted at 120° after one crystallization and at 146–7° after the second and subsequent purifications. This agreed with the value for the acetyl derivative of *p*-toluidine; consequently a benzoyl derivative was prepared. It was found to melt at 157° and the mixed melting-point with known benzoyl-*p*-toluidine showed an unchanged value. The difficulty was easily explained in the light of these numerical data. The unknown, although of constant boiling-point, was a mixture of toluidines, the solid *para* compound being dissolved in the liquid *ortho* isomer. The acetyl derivative was a mixture, but after several crystallizations from water the more soluble *ortho* compound was removed and pure acet-*p*-toluidine remained.

Manipulation of Small Amounts of Material.—When preliminary work indicates that an unknown is of questionable purity, it will be necessary to subject the compound to additional purification. Solids may usually be subjected to crystallization from suitable solvents, and liquids to fractionation. Distillation with steam, sublimation, and fractional precipitation are also occasionally of value. The methods used in previous organic laboratory work can therefore be applied but with suitable modifications to adapt the procedures to manipulation of relatively small amounts of material in such a way as to prevent mechanical losses.

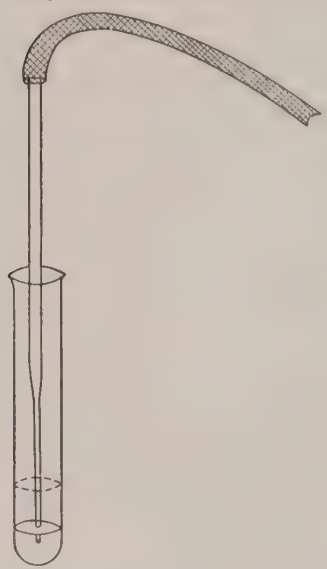


Fig. 3.

In general, it is necessary to use miniature apparatus. Many of the operations ordinarily requiring a separatory funnel can be carried out efficiently (see Fig. 3), by means of the suction pipette.

The latter is made by drawing out one end of an ordinary thin-walled glass tube and fire-polishing the ends. It should be of about 2 cc. capacity, graduated at $\frac{1}{2}$ cc. intervals, and equipped with a piece of narrow gum tubing of sufficient length that the tip of the pipette may be held at eye-level during the manipulation. The suction pipette is used not merely for separating liquid layers but also for measuring definite amounts of liquid organic reagents used in various tests. The method of pouring a portion of unknown or of an organic reagent from a test-tube or bottle and guessing at the quantity of material used, results not merely in a waste of material but also in poor results. Solid reagents are weighed on micro-platform or on horn-pan balances which permit rapid weighing with an accuracy of about 0.02 g.

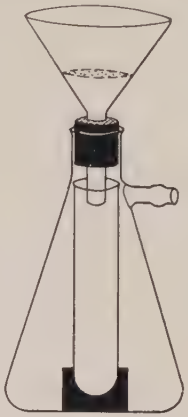


FIG. 4.

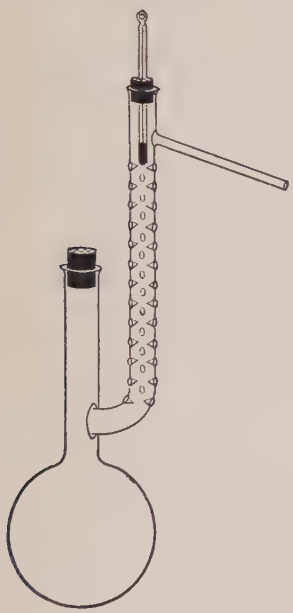


FIG. 5.

For suction filtration, particularly when the liquid is to be saved, the apparatus shown in Fig. 4 is of value.

Fractionations of small amounts of liquid that require a fractionating column are often very troublesome. The combined flask and column shown in Fig. 5 will often solve such a difficulty.

The examples given above will suggest a few of the directions in which effective work involving small quantities of material may be conducted without serious losses; excellent directions for the manipulation of small amounts of material in connection with the preparation of derivatives will be found in Mulliken, Vol. I. When only extremely small quantities of material are available, resort must be had to the methods of micro-analysis.

I. MELTING-POINTS

The ignition test will determine the advisability of taking a melting-point. Obviously it will be a waste of time to attempt taking melting-points on compounds which show no evidence of melting definitely when heated on platinum-foil. Most salts of acidic organic compounds with metals do not possess definite melting-points and the constants of the members which do melt before undergoing decomposition are not always available in the literature. Many hydrochlorides of organic bases possess reliable melting-points, but in general this class of compounds shows too little variation in melting-points among the individual members.

Compounds of high molecular weight often undergo decomposition before melting, and others may sublime. Many compounds undergo appreciable decomposition at temperatures near the melting-point and therefore the value obtained may vary somewhat with the rate of heating. This is noticeable with certain dicarboxylic acids (which ones?) and especially with polyhydroxy compounds, as with the sugars and some of their derivatives. A few types show two melting-points. Explain how this is possible.

A sharp melting-point is not necessarily a criterion of purity. A more reliable criterion is obtained by fractionally crystallizing a compound from two solvents of widely different types and redetermining melting-points of the various fractions. Small amounts of fusible impurities usually lower the melting-point.[1]

Mixed Melting-points are of Special Value in Qualitative Organic Analysis.—A small amount of the substance to be tested is *intimately mixed* with an equal portion of the known compound and the melting-point determined. If the two samples are identical, the melting-point will be unchanged, whereas the mixing of two different compounds possessing the same melting-point will usually, but not invariably, result in a different and usually a lower melting-point.[1]

The melting-point of a crystalline substance is that temperature at which the solid is in equilibrium with the liquid phase. The melting-points usually determined in the organic laboratory (and this is true also of most of the values recorded in the literature) are not *true* but *capillary melting-points.*

[1] For exceptions, see C. A. **14**, 57 (1920); also Finlay: The Phase Rule and Its Applications.

A small quantity of finely powdered solid material is placed in a capillary tube,[1] Fig. 6, and heated in a sulfuric acid or oil bath as indicated in Figs. 7 and 8. The open beaker method using a stirrer is preferable. The part of the capillary tube containing the substance should lie in contact with the bulb of the thermometer. As the temperature of the bath approaches the melting-point, the substance will often sinter and shrink from the walls of the tube; occasionally softening is noted as the melting-point is

Fig. 6.—Actual Size.

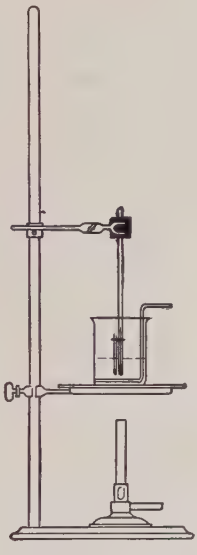


Fig. 7.

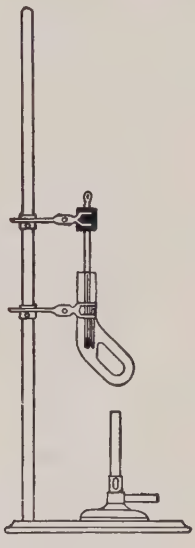


Fig. 8.

approached; finally the material liquefies, sometimes gradually over a range of several degrees but more often quite sharply.

For example, a given unknown was observed to soften at 138°,

[1] A light-walled glass tube 15 mm. in diameter is heated uniformly over about 3 cm. of its length and drawn out into meter lengths of uniform bore. The capillaries are then cut into convenient lengths, sealed at one end and protected from contamination by storage in a dry stoppered test-tube. For a determination of melting-point a 5 mm. layer of material is placed in a tube. Vibration of the latter by means of a file will be of aid in causing the material to settle rapidly to the bottom of the tube in a compact layer.

When a sulfuric acid bath is used, the capillary tube (if of uniform bore and of sufficient length as shown in Fig. 6) will adhere to the thermometer by capillary attraction. When an oil-bath is used, a small rubber band may be used to fasten the capillary.

actual liquefaction was noted at 142° and the substance was completely melted at 142.5°. It is customary to record these data in the following manner: *m.p.* 142–142.5° *c.* (softens at 138°). The letter *c* indicates that the thermometer reading has been corrected [1] for stem exposure.

In general, it is advisable to make two determinations; in the first one the bath may be raised quite rapidly and the melting-point located within a range of about 5°. The bath is then allowed to drop 10°–20° below the melting-point, a new charged capillary tube attached to the thermometer, and the temperature of the bath raised gradually and uniformly (stirring). As the actual melting-point is approached, the temperature of the bath should be raised at the rate of about 1° per five to ten seconds.

Question: A sample of *o*-phthalic acid was found to melt at 185°–195° when the capillary tube was placed in the cold bath and the temperature gradually raised to the melting-point. The bath was then allowed to cool to 175° and the melting-point of a second portion determined. The second value was found to be 200°–205°. Explain these variations.

For melting-point determinations in the neighborhood of 300°, it is advisable to use either (*a*) a sulfuric acid bath containing about 40 per cent of potassium acid sulfate or (*b*) a cotton-seed oil bath containing about 10 per cent of beeswax. In all work of this kind even at low temperatures, particularly where sulfuric acid is used, special precautions must be observed to prevent accidents. The work at the higher temperatures must be conducted under a hood.

Many organic compounds that are met in the form of liquids may be solidified by chilling in a freezing mixture. In such cases true rather than capillary melting-points are determined. A 1 or 2 cc. portion of the liquid is placed in a test-tube and a thermometer placed directly in the liquid. The tube is then placed in a freezing

[1] The formula often used is: Correction $= +N(t-t')0.000154$; in which N represents the number of degrees on the stem of the thermometer from the surface of the bath to the temperature read, t the temperature read, t' the average temperature of the exposed mercury column, and 0.000154 the apparent coefficient of expansion of mercury in glass.

Since this correction is of questionable accuracy under the usual laboratory conditions, it is advisable for each student to calibrate a 360° thermometer against a standardized laboratory thermometer. The two instruments are placed side by side in the bath shown in Fig. 7 and comparisons made over the entire temperature range at 25° intervals. It is essential in this case to use a slightly larger bath and also a stirrer.

mixture and the walls of the tube scraped with the tip of the thermometer. Very often persistent supercooling will be noted but after a compound has once been solidified an accurate melting-point value may be determined.

II. BOILING-POINTS

The usual method of determining boiling-points when appreciable amounts of liquid are available is to actually distill a 5–10 cc. portion of the material. This procedure furnishes not merely a boiling-point but also something of more value in ordinary work, namely, a boiling-point-range. The operation differs from the usual distillation procedure only in the use of smaller amounts of material and miniature apparatus.

The small 10 cc. flask is placed upon a square piece of asbestos board which contains a perforation of about 2 cm. diameter. A small flame is used so as to prevent superheating,* but care must be taken to prevent fluctuations in the thermometer reading due to variable cooling of the vapors in the neck of the flask. The bulb of the thermometer should be placed near the outlet of the flask and naturally the temperature reading is not taken until the mercury of the thermometer has been given time to come to the temperature of the vapor. Because of the small amount of liquid distilled it is necessary to distill slowly. The type of condenser used (air or water-cooled) depends upon the boiling-point of the liquid being distilled, but should be of small size so as to prevent excessive loss of the distillate. Very high-boiling liquids may be collected directly into a test-tube receiver since the quantity of distillate is so small. When some suggestion is at hand in regard to possible decomposition upon distillation, it is necessary to test a cubic centimeter of material by heating in a small test-tube before subjecting the main portion of the sample to a high temperature.

Substances which boil with decomposition under ordinary pressure may usually be distilled under diminished pressure. Usually this will not be necessary when dealing with an individual compound since other constants and particularly the constants of derivatives may be relied upon. For the separation of certain liquid mixtures which contain ingredients that may be distilled only under reduced pressure, it is necessary to resort to this modified method.

* Particularly when distilling low-boiling liquids the use of a chip of porous plate is advantageous.

The boiling-points of small portions of material (about $\frac{1}{2}$ cc.) may be determined in the apparatus shown in Fig. 9. The test-tube and attached thermometer are heated in the usual melting-point bath equipped with a stirrer. The test-tube contains a glass tube, 4 mm. in diameter, which acts as a condenser; the lower end (8 mm.) is sealed off but is open at the end and immersed to a depth of about 4 mm. in the liquid under examination. The bath is heated to slightly above the boiling-point of the unknown until the last traces of air have been driven from the lower open end of the condenser tube. As the temperature of the bath is now slowly lowered it is noted that vapor bubbles cease to emerge from the lower end. Soon after this, the liquid tends to slowly draw back into the tube. The temperature at which the level of the liquid within the tube is the same as that outside is taken as the boiling-point; i.e., the temperature at which the liquid is in equilibrium with the vapor.

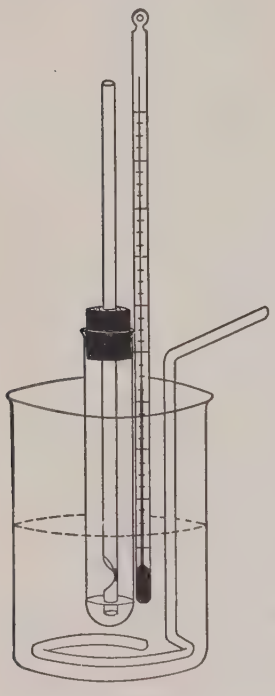


FIG. 9.

In the hands of the beginner, the method described above is not particularly reliable and it is therefore necessary to test out the apparatus on several compounds of known boiling-points before relying upon the results obtained with unknown compounds. The method is adaptable only to work with pure compounds and is therefore of limited value.

III. SPECIFIC GRAVITY

The density of liquid unknowns is determined most conveniently by means of the specific gravity tube [1] shown in Fig. 10.

The tube is standardized by weighing it, first empty and again

[1] These tubes are easily prepared by sealing one end of a thick-walled glass tube of 3-mm. diameter and blowing a bulb of the form shown.

after it is filled with distilled water and the level of the latter adjusted to the mark at a temperature of 20°. The dry tube should be kept in a clean box with a card showing (*a*) its weight filled with water at 20°, and (*b*) its weight when empty. In all subsequent work one filling and weighing will be sufficient to determine the specific gravity of the unknown.

In determining the specific gravity of an unknown, fill the tube to slightly above the etched mark by means of a glass tube drawn to a capillary of such diameter that it may be inserted through the narrow neck to the bottom of the tube. Place the tube and its contents in an upright position into a small beaker containing water at 20°. After ten minutes, adjust the level of the liquid to the reference mark by means of the capillary pipette, dry the tube, and weigh it. The specific gravity (d_{20}^{20}) will be equal to the weight of the sample divided by the weight of the same volume of water. Weighings are taken only to the third decimal place.[1]

FIG. 10.—Actual size for tube of about 0.6 cc. capacity.

Before returning the tube to the box, the liquid is recovered by withdrawing it with the capillary pipette and the tube is cleaned first with alcohol and with ether. Finally, the ether vapor is removed by drawing, not blowing, air through the pipette.

OTHER PHYSICAL CONSTANTS

Melting-point, boiling-point, and specific gravity represent the three constants of organic compounds that are determined as a routine procedure. Other constants, such as refractive index, optical rotation, quantitative solubility determinations, etc., are applied in later stages of an analysis if found to be of sufficient importance to aid in the differentiation between a number of possibilities. Molecular weight determinations are required only in exceptional instances.

The Index of Refraction (n) is the ratio of the sine of the angle of incidence to the sine of the angle of refraction (ratio of the

[1] Greater accuracy is not justified because of the questionable purity of many unknowns. A temperature of 20° has been chosen not only because it is near room temperature but also because many of the results in the literature have been reported at 20°.

velocity of light in air to that in the substance under examination); it may be read directly by means of the Abbé refractometer, which is the most convenient form of instrument for use in the qualitative laboratory.

The Specific Rotation of an optically active compound is determined by means of the polariscope. The specific rotation $\left[\alpha\right]_D^t$ observed by sodium light at the temperature t is calculated according to the formula:

$$\left[\alpha\right]_D^t = \frac{100\,\alpha}{l \times c}$$

where α represents the observed angle of rotation (either + or −), l the length in decimeters of the column of liquid in the polariscope tube, and c the number of grams of active substance in 100 cc. of solution.

Molecular Weight Estimations may be made by a variety of methods, the most important of which are the cryoscopic, the ebullioscopic, and the vapor density methods. The first mentioned method, based upon the accurate determination of the depression of the freezing-point of a known solvent following the introduction of a known weight of solute, is generally applicable and is used most often by the organic chemist. The molecular weight (M) is calculated according to the formula:

$$M = \frac{c \times p}{\Delta}$$

where c is a constant for the particular solvent used, p is the number of grams of the unknown per 100 g. of solvent, and Δ is the depression of the freezing-point. A similar formula is used for calculation of molecular weights based upon the elevation of the boiling-point of a liquid due to the presence of a non-volatile dissolved substance. In the latter instance, the constant c' is substituted for c and Δ now represents the rise in boiling-point.

In connection with the identification of organic compounds that have been previously characterized, the estimation of equivalent weights is of more value that that of actual molecular weights. This is done by estimating quantitatively some typical element or reactive group. Such methods are discussed in Chapter XI.

The Value of Physical Constants when Used in Connection with Class Reactions.—Unnecessary group tests are often applied

by the beginner when the desired specific information may be gained from a consideration of the physical constants of an unknown. Examples will be given from among the halogen derivatives of the hydrocarbons but similar applications may be made to other classes of compounds.

When a halogen compound possesses a boiling-point below 125° at 760 mm., the unknown cannot be an aromatic compound.

When an organic bromine derivative boils below 150°, it must be aliphatic. Similarly, an iodine derivative with a boiling-point below 180° must be aliphatic. In these instances, sulfonation and other tests for differentiation between the aliphatic and aromatic series are superfluous. (Note that the above statements are not limited merely to halogen derivatives of hydrocarbons, but apply to all organic halogen compounds.)

When an organic chlorine derivative boils below 175° but possesses a specific gravity of more than $1.4^{20°}$, then it is an aliphatic compound; similarly, bromine compounds boiling below 200° but possessing specific gravities of more than $1.6^{20°}$ must be aliphatic compounds.

Explain the statements given above and be prepared to cite evidence either for or against these generalizations. Why would it be unsafe to base analogous statements upon melting-point data?

ANALYSIS FOR THE ELEMENTS

Test the unknown for an inorganic residue by igniting a small amount of material in a crucible. If a residue is left, examine it by the usual methods used in inorganic qualitative analysis. Residues from calcium and barium salts will be detected readily. Sodium and potassium salts will leave fusible residues of the corresponding carbonates which may be overlooked by a careless observer. Some inorganic materials may prove to be volatile (give examples), whereas others may leave black residues of either oxide or reduced metal (give examples). Usually, however, black residues are due to the presence of carbonaceous matter which is removed only upon prolonged heating.

Many fairly pure compounds leave a trace of residue upon ignition and in cases of doubt this may be weighed in order to determine whether it represents an appreciable portion of the total weight.

ANALYSIS FOR S, N, Cl, Br, AND I

Very few organic compounds contain these elements in such a form that they may be tested directly by the methods of ion analysis; fusion with metallic sodium, however, decomposes the organic substance according to the following scheme:

$$[\text{C, H, O, N, S, Cl, Br, I, etc.}] + \text{Na}_x \xrightarrow{\text{heat}}$$

$$\text{Na}_2\text{S, NaCN, NaCl, NaBr, NaI, Na}_2\text{O, C, CO}_2\text{, H}_2\text{O, etc.}$$

In the fusion mixture, sulfur may therefore be detected by the usual tests for sulfide ions, nitrogen by the tests for cyanide, and the halogens by the usual familiar methods. Rarely, when sulfur and nitrogen are both present, a trace of NaCNS may also be formed and may be detected by the red coloration given with ferric chloride after acidification.

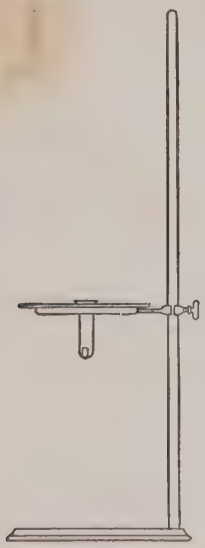


Fig. 11.

Directions for the Sodium Decomposition.—Place a piece of clean metallic Na the size of a very small pea into a 2-inch test-tube suspended through a piece of asbestos board as shown in Fig. 11. Add a little of the material (one drop of a liquid or a few fragments of a solid) and heat the tube with a small flame, not only until the sodium melts, but until the vapors of sodium form a layer $\frac{1}{2}$ inch in height. Allow three drops of the unknown, if liquid, or an equivalent quantity of fragments, if solid, to fall at intervals of one or two seconds directly upon the fused sodium without touching the sides of the tube. (Precaution!) Heat the reaction-mixture strongly so as to oxidize most of the residual sodium as well as to remove volatile organic decomposition products. By means of a pair of tongs, lower the hot tube into a small beaker containing 10 cc. of water. (Special precaution!) The tube is merely touched to the surface of the water and then raised out of the liquid but held in the beaker in such a manner that the heavy glass of the beaker will be between the tube and the eyes of the operator. Momentary contact with water will cause the hot tube to crack and traces of unreacted sodium will be destroyed by spon-

taneous burning without the dangers of a hydrogen explosion. (Demonstration by instructor.) The cooled tube is now tapped against the inner side of the beaker and the lower cracked part allowed to drop into the water. The solid particles are broken up with a stirring rod, the solution heated to boiling and filtered. The filtrate, which should be colorless, is reserved for the subsequent tests.

A. Sulfur Test.*—To 1 cc. of the filtrate made slightly acid with acetic acid, add a few drops of lead acetate reagent. A black precipitate of PbS shows the presence of sulfur.

B. Nitrogen Test.*—Boil 3 cc. of the *alkaline* stock solution for two minutes with 5 drops of $FeSO_4$, and 1 drop of $FeCl_3$ solution. Cool and acidify carefully with HCl. The precipitate of iron hydroxide should dissolve readily, otherwise the solution should be warmed very gently. A clear yellow solution indicates a negative nitrogen test; a blue precipitate indicates a positive test. A blue or greenish-blue solution suggests the presence of nitrogen but indicates that the original sodium decomposition may have been poor. The precipitate of Prussian blue shows up best when it is collected and washed upon a white filter paper. If iodine is present, the filter is washed with alcohol to dissolve out the iodine. In the presence of sulfides, it will be advisable to add enough $FeSO_4$ solution to completely precipitate the sulfur ions, filter off the FeS, and proceed as above.

Write equations illustrating the formation of Prussian blue.

C. Tests for Halogen. (*a*) *General Test.*—Acidify 2 cc. of the stock solution with dilute HNO_3 and boil well to expel any H_2S or HCN if present. Add $AgNO_3$ solution. A precipitate denotes the presence of halogens. Also apply the Beilstein copper-oxide-wire test to the original unknown.

(*b*) *Tests for Bromine and Iodine in the Presence of Each Other and the Other Halogens.*—Acidify 2 cc. of the stock solution with H_2SO_4 and boil gently to drive off H_2S. Add not more than $\frac{1}{4}$ cc. of carbon tetrachloride and finally a drop of a solution of freshly prepared chlorine water. Shake after the addition of each drop. If iodine is present, the carbon tetrachloride will be colored purple. Continued additions of chlorine water will cause the iodine color to disappear, due to the formation of the iodate, and if bromine is present the carbon tetrachloride will become colored

* These tests may be supplemented by the addition of K_2F_2 in the nitrogen test and the use of sodium nitroprusside in the sulfur test. Cf. Fisher's Laboratory Manual of Organic Chemistry, Wiley, 1924, pp. 112–113.

brown at this stage. Be careful to add the chlorine water slowly or these colors may be missed.

(*c*) *Tests for Chlorine in the Presence of Other Halogens.*—Acidify 2 cc. of the stock solution with a few drops of acetic acid, add excess of PbO_2, and boil gently until all the Br_2 and I_2 are liberated. Dilute and test for $\overline{Cl}$ by the addition of HNO_3 and $AgNO_3$. A faint chlorine test may be due to a trace of chlorine either in the metallic sodium or in the glass of the test-tube used for the fusion, or in the PbO_2. A blank test should be run.

Beilstein CuO Test for Halogen.—This test is applied to the original unknown. A copper wire of small diameter is heated in the flame until no trace of green color is noted. The cooled wire is dipped into a small portion of the substance and again heated. A green color imparted to the flame, sometimes only a momentary flash, is due to the volatilization of copper halide.

The above tests are the only ones applied in a routine way to the unknowns met in the present course. Carbon and hydrogen may be detected by heating the substance in a dry test-tube with ignited CuO and identifying the moisture and carbon dioxide generated. Such a test is usually superfluous, since abundant amounts of elementary carbon may be observed in the sodium decomposition reaction, and special tests for hydrogen are unnecessary for the purposes of identification of unknowns.

Phosphorus may also be detected in the filtrate from the sodium decomposition, provided that a 1 cc. portion of the filtrate be oxidized by boiling with a little concentrated nitric acid and subsequently tested with ammonium molybdate reagent. A more reliable test which is applicable also to quantitative work consists in fusing the organic compound (if non-volatile) with sodium carbonate and a small amount of potassium nitrate in a nickel crucible. The melt is dissolved in acid and tested with molybdate reagent in the usual manner.

The Carius sealed tube method is capable of yielding excellent results but is ill-suited to routine work because of the time factor. In special instances, however, it may be necessary to apply the method which with slight modification is applicable to the quantitative as well as qualitative estimation of a variety of elements. A sample weighing 0.1 gram is heated in a sealed bomb tube with 1 cc. fuming nitric acid (sp. g. 1.48) at a temperature of 200–300° during several hours. Sulfur, arsenic, and phosphorus are converted into sulfuric, arsenic, and phosphoric acids respectively, chlorine and bromine will be present partly as hydrochloric and hydrobromic acids and partly as free halogen, iodine as iodic acid, and metals will be present as nitrates. Because of considerable pressure developed, great care must be taken not only in heating but especially in opening the bomb-tube. The detailed directions in Gattermann's Laboratory Manual should be studied carefully before undertaking this dangerous operation.

A satisfactory method for treatment of organic arsenic consists in digestion with sulfuric acid (in the presence of starch) by analogy to the Kjeldahl method for nitrogen. Qualitatively the arsenic may be detected as sulfide and quantitatively by iodimetric methods. (J. Chem. Soc. **109**, 1356 (1916)). The Marsh test serves for the detection of traces of arsenic.

Mercury in organic combination may often be converted into inorganic form by digestion with hydrochloric acid, filtration from insoluble impurities and precipitation with hydrogen sulfide. See also Whitmore: Organic Compounds of Mercury, A. C. S. Monograph, pp. 361–367 (1921).

For references concerning these and other specialized tests the list mentioned at the end of Chapter V should be consulted.

CHAPTER VIII

LABORATORY WORK ON THE SOLUBILITY BEHAVIOR OF ORGANIC COMPOUNDS

The analytical procedure presented in this course has been systematized primarily on the basis of solubility behavior. Before proceeding with the application of the scheme, it is advisable to devote one or two laboratory periods to the study of the solubility behavior of known compounds and to the comparison of predicted solubility values with those actually determined experimentally.

Determine the solubility behavior of a number of typical organic compounds, selecting members from various important homologous series. (A suggested list is indicated on page 129.) Test the solubilities in the following reagents:

1. Water.
2. Ether.
3. Dilute acid (5 per cent HCl).[1]
4. Dilute alkali (5 per cent KOH). Note odor of evolved gases.
5. Cold concentrated H_2SO_4 [1] (if the compound is insoluble in tests 1, 2, 3 and 4).

Solubility tests are applied at room temperature (20°–25°). Observations of value may be made by determining solubility behavior in hot solvents but *for purposes of classification the results obtained at room temperature are the ones desired.* The action of hot acid or alkali will be studied subsequently in connection with the homologous tests.

Amount of Material Required in Solubility Tests.—The quantity of the unknown used in a solubility test will naturally depend upon the amount available. Usually it is convenient to use 0.10 g.

[1] Tests applied to any evolved gases are also of value. Caution must be observed since poisonous products like hydrocyanic acid, carbon monoxide, and cyanogen may occasionally be encountered.

of a solid [1] or 0.2 cc. of a liquid for 3 cc. of solvent. The same portion of substance may be used, however, in several solubility tests and occasionally practically the entire quantity of material may be recovered for use in subsequent work. When a particularly rare substance is under investigation, correspondingly smaller amounts of substance and solvent must be used and special thought be directed to the question of recovery.

Solubility in Water and in Ether.—A 0.10 g. portion of a solid unknown is treated with successive 1 cc. portions of water until 3 cc. have been added. If the compound does not dissolve in the ratio of 1 : 20 or 25, it is designated " insoluble in water." The substance if solid must be finely powdered so as to eliminate the possibility of a verdict of insoluble when in reality a mechanical difficulty is responsible for the decision. If the substance appears to be insoluble, the suspension may be warmed gently. If solution occurs, the test portion is again cooled and shaken vigorously to prevent supersaturation upon cooling.

When dealing with liquid unknowns, 0.2 cc. of the substance, delivered from the graduated pipette, is added to 3 cc. of water. In this case equilibrium is attained quickly and the substance is called insoluble if it does not dissolve in the proportion of 1 : 10 or 15. The student should not be misled, however, by the presence of a trace of insoluble impurity in an otherwise soluble substance. Give a theoretical explanation justifying a different standard of solubility for solid in comparison with melted compounds.

Whenever a compound dissolves in water, test the aqueous solution with litmus paper. In the case of liquids that are not completely miscible, note their specific gravities in comparison with water and record this data in your notes (sp. gr. >1 or <1).

Solubility tests in ether are carried out in a manner analogous to that described for the water solubility tests. Compounds falling in the borderline between what has been arbitrarily designated " soluble " and " insoluble " should be sought in more than one group of the solubility table; often the substance will be found classified in both places. The ether solubility test may often be applied in conjunction with the tests in water, dilute acid, or

[1] It is advisable to weigh this material to within 1 centigram. If this is not done, the beginner is liable to use as little as 0.02 g. of a light fluffy substance and on the other hand in dealing with heavy crystals a correspondingly large error is liable in the opposite direction. Small trip balances accurate to .01 g. should be available for this purpose.

alkali, provided that suitable recognition be given to the possible reactions of the unknown with either acid or alkali.

Solubility in Dilute HCl.—In this test, it is advisable to utilize the same portion of unknown used in the water test. The proper amount of substance thus will be available, either dissolved or suspended in 3 cc. of water. To this solution or suspension add *gradually* with shaking $\frac{1}{2}$ to 1 cc. of 20 per cent HCl. The final solution thus will contain about 5 per cent of HCl. The acid is added gradually ($\frac{1}{4}$ cc. at one time) for the reason that certain organic bases form hydrochlorides that are only sparingly soluble in the excess of HCl. Such compounds may prove to be soluble after $\frac{1}{4}$ cc. of acid has been added but may be insoluble in the excess.

Question.—An unknown is soluble in water but a precipitate is formed when HCl is added. What can be predicted concerning the unknown?

Solubility in Dilute KOH.[1]—The material used in the water and in the acid solubility test may often be recovered and utilized for solubility in dilute KOH. When dealing with substances sparingly soluble in water (1 : 200 or less), it is convenient to use directly the solution or suspension from the preceding test. The acid solution is exactly neutralized by the addition of $\frac{1}{2}$ to 1 cc. of 30 per cent KOH, cooled to room temperature, and a further quantity ($\frac{1}{2}$ to 1 cc.) of KOH added *gradually* with cooling.

Nitrogenous compounds that are found to be soluble in water but insoluble in ether should be tested for the evolution of ammonia or volatile amines when treated with alkali. This test is applied by placing a small amount of material on a watch-glass, moistening with strong KOH and noting the odor. The beginner, however, should not rely upon his olfactory sense for differentiation between ammonia and the volatile organic amines.

Question.—An unknown is soluble in water but a precipitate is formed when KOH is added to the aqueous solution. What can be predicted concerning the unknown?

Solubility in Cold Concentrated H_2SO_4.—The sulfuric acid test is of value in differentiating between Groups V and VI. Compounds falling in Groups I, II, III, and IV, as well as indif-

[1] Potassium hydroxide is used here in preference to sodium hydroxide because the sodium salts of certain organic acids and phenols are sparingly soluble, particularly in excess alkali. Hydrochloric acid has been used in preference to sulfuric for the reason that the hydrochlorides of organic bases are often more soluble than the sulfates.

ferent compounds containing N, S, etc., need not be subjected to the test in so far as classification is concerned. Since the test may give information of value apart from classification data (evolution of gases, charring, production of color, etc.), it is advisable to apply the test to each unknown examined. The student must refrain from placing any special reliance upon the numerous sulfuric acid color tests reported in the literature, since these are often greatly modified by traces of impurities. The test must be applied to the dry substance and *cold* concentrated acid must be used. Liquid compounds in Group V will usually dissolve quickly but solid compounds must be finely powdered and may require several minutes for solution. The applications and limitations of the test have been discussed in Chapter II.

The following compounds are suggested for solubility work. All materials must be used sparingly.

Class			Individual selected
Hydrocarbons and Halogen derivatives	Saturated aliphatic		Ligroin
			Ethyl bromide
	Aromatic		Toluene
			Bromobenzene
	Unsaturated		Amylene
Ethers	Aliphatic		Ethyl ether
	Aromatic		Anisole
Esters	Aliphatic (low mol. wt.)		Ethyl acetate
	Aromatic		Ethyl benzoate
Anhydride			Acetic anhydride
Acids	Aliphatic (low mol. wt.)		Acetic acid
	Aromatic	Monobasic	Benzoic acid
		Dibasic	Phthalic acid
		Amphoteric	Anthranilic acid
Ketones and Aldehydes	Aliphatic		Acetone
	Aromatic		Acetophenone
Alcohols			Amyl alcohol
			Ethyl alcohol
			Benzyl alcohol
Phenols			Phenol
			β-Naphthol
Nitro compounds			Nitrobenzene
			Trinitrotoluene
Nitrile			Benzyl cyanide

Amines, Amides, Imides, and Ring N	Primary amines	Aniline Benzidine
	Tertiary amine	Dimethyl aniline
	Negatively substituted (amide)	Acetanilide
	Negatively substituted (imide)	Phthalimide
	Ring nitrogen	Quinoline Uric acid
Sulfonic acids, Salts, and Carbohydrates		Ammonium benzoate Sodium benzoate Sodium benzene sulfonate *p*-Toluidine hydrochloride Sucrose

Supplement the above list with other typical compounds in which you are interested and in each case compare your results with the proposed solubility table at the end of this text. With the aid of your instructor apply any additions and corrections to this table. Do not proceed with laboratory work on identification of unknowns until you feel confident in being able to predict the solubilities of common organic compounds from the corresponding formulas without resorting to actual laboratory test; in other words, do not attempt to memorize any part of the Solubility Table, but instead, know the generalizations upon which the table is based.

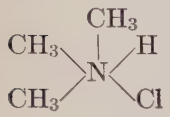
Record solubility data in the following manner:

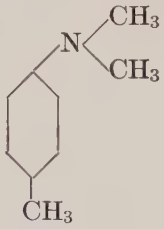
Substance	Solubility in					Solubility Group
	Water	Dilute HCl	Dilute KOH	Conc. H_2SO_4	Ether	
Piperidine hydrochloride	+	+	+ (ammonia-like odor)	Evolution of HX	−	II
Phenyl salicylate	−	−	+	+	+	IV
Iso-amyl ether	−	−	−	+	+	V
m-Xylene	− (sp. g. <1)	−	−	−	+	VI

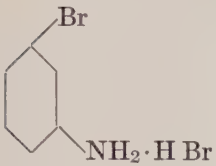
Class-room Exercise.—Predict the solubility behavior of the following compounds and be prepared to give in each case the generalizations that lie at the basis of your answers.

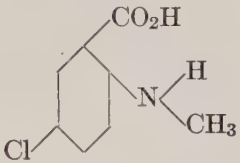
$CH_2OH \cdot (CHOH)_3 \cdot CO_2H$ $CH_3 \cdot CH_2 \cdot CO \cdot CH_3$

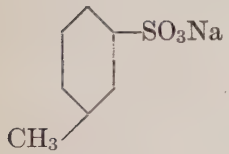
$CH_3 \cdot (CH_2)_2 \cdot CHCl \cdot CO_2 \cdot (CH_2)_3 \cdot OH$

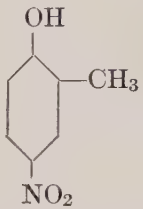


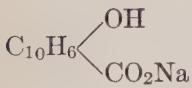






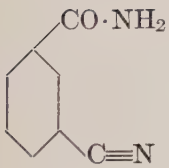


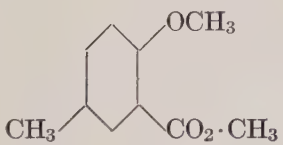


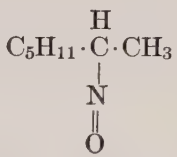


$C_6H_5 \cdot CH_2 \cdot NH \cdot SO_2 \cdot C_6H_5$

$C_6H_5 \cdot C_2H_5$







CHAPTER IX

LABORATORY WORK ON CLASSIFICATION REACTIONS OF ORGANIC COMPOUNDS

In the following experiments, note carefully and record immediately in your laboratory note-book all observations. Attention should be directed especially to the following phenomena: Heat effects, evolution of gases, changes in physical state (as for example the conversion of a liquid to a solid), changes in solubility, odors, color changes, etc.

All observations should be recorded in a permanent laboratory note-book in the following manner:

(*a*) Observations,

(*b*) Reactions, written structurally,

(*c*) Conclusions.

Most of the experiments will consist of review work and the reactions may be interpreted with the aid of the knowledge gained in an elementary course in organic chemistry. The discussion in Chapters II, III, IV, and V will prove of value but the student is expected to use also more advanced reference books. Special emphasis will be placed upon the interpretation of the reactions and the drawing of proper conclusions therefrom for the purposes of organic analysis. In doing this for any one experiment, it will often be necessary to utilize the results of other experiments. The limitations of the tests and the exceptions must be considered also in summarizing the results. No equations are required for experiment 1.

EXPERIMENT 1

Ignite on a strip of platinum foil over a small flame a small amount (0.1 g.) of each of the following substances: (*a*) ligroin, (*b*) toluene, (*c*) benzoic acid, (*d*) ethyl ether, (*e*) glycerol, (*f*) ethyl alcohol, (*g*) trinitrotoluene, (*h*) amyl alcohol, (*i*) sodium

acetate, (*j*) barium benzoate, (*k*) ammonium benzoate, (*l*) starch, and (*m*) urea.

Ignition is the first test applied to any unknown compound. If the compound does not burn, what test should be applied? Note that certain organic compounds burn with the production of a large quantity of soot, while others burn merely with a luminous and sometimes with a non-luminous flame. Can any generalization be drawn in regard to this behavior? Review the results of the "burning tests" applied to methane, ethylene, and acetylene in your elementary course. Note that the luminosity of the flame is somewhat dependent upon the quantity of material ignited.

Is a residue left on ignition? If so, is it fusible or non-fusible? Is it an alkaline residue? Is it a carbonate? What is its color? Certain fusible residues may form a thin glassy coating on the platinum and thus escape detection by the beginner. Certain substances like starch may contain sufficient impurity to leave a trace of residue. Usually such a residue is easily differentiated from the amount left from the ignition of a typical salt.

If the compound is a solid, does it possess a melting-point? If so, predict its melting-point to within about 25°. Most salts, and substances which decompose or sublime without melting need not be subjected to actual melting-point determinations.

The odor of compounds upon ignition is often suggestive to the experienced analyst but care must be observed by the beginner because of the possibility of meeting toxic products.

TESTS FOR UNSATURATION

EXPERIMENT 2

Dissolve 0.2 cc. of amylene in 2 cc. of carbon tetrachloride and add *gradually* a 5 per cent solution of bromine in carbon tetrachloride until a bromine color remains for about one minute.

Repeat this experiment using in place of amylene equal weights of (*a*) phenol, (*b*) toluene, (*c*) allyl alcohol, (*d*) ethyl alcohol, (*e*) maleic or cinnamic acid, (*f*) acetophenone. Because of the limited solubility of cinnamic acid in carbon tetrachloride, 2 cc. of chloroform should be used as a solvent.

Why is carbon tetrachloride used as a solvent? How may one differentiate between addition of bromine and substitution by bromine? Suggest an experiment for determining whether addition is taking place as well as substitution. Would aniline respond to this test? What classes of compounds are readily substituted by halogens? Certain ethylene derivatives add bromine very slowly. May such exceptions be predicted?

EXPERIMENT 3

To 3 cc. of sodium carbonate (5 per cent) solution, add 0.2 g. of amylene and then drop by drop with shaking a 2 per cent solution of potassium permanganate. Continue the addition until the permanganate color is no longer destroyed.

Repeat this experiment using in place of amylene equal weights of (*a*) toluene, (*b*) cinnamic or maleic acid, (*c*) benzoic acid, and (*d*) salicylic acid or phenol.

In this experiment, it is necessary to differentiate between a slight reaction due to impurities and a typical oxidation. For example, the impurities in technical toluene may react with a few drops of the permanganate solution but a reaction such as the oxidation of the side-chain to carboxyl would require 30 cc. of reagent.

Does the permanganate test serve to detect those double unions that react only slowly toward addition of bromine? Does the bromine test (Exp. 2) serve to modify conclusions drawn from Experiment 3?

Test also benzaldehyde, acetone, glycerol, and ethyl alcohol.

Under what conditions may copper acetylide be prepared? Is the formation of explosive metallic derivatives typical of all tri-bonded compounds?

SATURATED HYDROCARBONS

EXPERIMENT 4

To $\frac{1}{2}$ cc. of cyclohexane add $1\frac{1}{2}$ cc. of 20 per cent fuming H_2SO_4. Mix by shaking at first gently and then more vigorously. Allow the mixture to stand for several minutes to determine whether solution has taken place. Repeat the experiment using in place of cyclohexane (*a*) toluene or benzene, and (*b*) *purified* ligroin.

The sign of reaction is the generation of heat and complete solution of the compound without excessive charring. Occasionally it is desired to separate the sulfonation product. This may be done by pouring the reaction mixture into 10 cc. of water, filtering (from what?), and saturating the filtrate with NaCl. Why is the above test not applied when the unknown dissolves in cold conc. H_2SO_4 or when it undergoes decomposition with conc. H_2SO_4?

Will the above differentiation apply also to the halogen derivatives of the hydrocarbons? If in doubt, apply the test to ethylene bromide and bromobenzene respectively.

How may nitration be used to differentiate between aliphatic and aromatic hydrocarbons? How may the Friedel and Crafts Reaction be employed for this purpose?

EXPERIMENT 5

To ½ cc. of benzene add 1 cc. of dimethyl sulfate. (Precaution!) Repeat this experiment using in place of benzene an equal volume of ligroin, petroleum ether, or kerosene.

The reagent must not contain free sulfuric acid. Because of the reported toxicity of dimethyl sulfate, great care must be taken in handling it The products from the above experiments are poured into 1 : 1 ammonia water to decompose the sulfate. If a drop of the ester touches the skin, the latter should be washed with water and then with ammonia solution. The toxicity of dimethyl sulfate may possibly be due to a methylation of hæmoglobin.

HALOGEN COMPOUNDS

EXPERIMENT 6

To 3 cc. of *alcoholic* silver nitrate solution, add one drop of benzyl chloride. After one minute heat the solution to the boiling-point and observe.

Repeat the experiment, using in place of benzyl chloride one drop of each of the following compounds: (*a*) benzoyl chloride,[1] (*b*) bromobenzene, (*c*) ethyl bromide, and (*d*) chloroform or carbontetrachloride.

In actual identification work when elementary analysis has shown the presence of halogen, this test should be preceded by the usual aqueous silver nitrate test for ionic halogen. Occasionally also free halogen acid may be present as an impurity.

Halogen compounds show a similar distinction when boiled with alcoholic NaOH or KOH. How should this test be applied and why is alcoholic alkali used in place of the aqueous solution?

EXPERIMENT 7

To ½ cc. of water, add cautiously a few drops of acetyl chloride.

Repeat the experiment, using in place of acetyl chloride two drops of benzoyl chloride.[1]

Repeat both parts of the experiment, using ½ cc. of aniline in place of water.

Would halogen compounds like ethyl bromide and benzyl chloride react in a similar manner with aniline? What may be said about the relative reac-

[1] The vapors of benzoyl chloride are very irritating to the eyes. Destroy all benzoyl chloride residues with conc. NH_3 before pouring them into the sink.

tion velocities of alkyl halides in comparison with the reactivity of the acyl halides? How will substitution by halogen affect the physical and chemical properties of the various classes of compounds listed in the solubility table?

ALCOHOLS, PHENOLS, ACIDS, ETC.

EXPERIMENT 8

Add small slices of metallic sodium to 1 cc. of pure amyl alcohol until no more dissolves. Cool the solution. Repeat the experiment, using toluene, acetone, amyl ether, etc. How can the test be applied to a solid substance?

Why does ordinary ethyl ether react readily with metallic sodium? Some esters, ketones, amides, etc., also react. Write the equation for the reaction between sodium and acetoacetic ester. Some high-molecular-weight compounds that are also very feebly acidic may not dissolve in dilute aqueous alkali. Such compounds are often detected by dissolving in alcohol and adding a little alcoholic sodium ethylate. (See Problem 3.) The sodium test is never applied to compounds in Group IV; its main use is in differentiating between alcohols and ethers and, because of the interference by moisture, it is of limited value.

Would halogen compounds ever interfere with the sodium test?

EXPERIMENT 9

Add three $\frac{1}{2}$ cc. portions of acetyl chloride to (*a*) 1 cc. of ethyl alcohol and (*b*) to 1 g. of phenol. After one minute pour the mixtures separately into 5 c.c. of water (Caution!). With the suction pipette, separate the reaction product from (*b*) and test its solubility in dilute NaOH to determine whether the product is still acidic.

Into a 2-oz. g.s. flask, place 2 cc. of ethyl alcohol dissolved in 10 cc. of water. Add 2 cc. of benzoyl chloride and 10 cc. of 20 per cent NaOH solution. Shake the mixture steadily for five minutes. This test indicates an alcohol, phenol, or hydroxy acid.

What would happen if alcohol were omitted in the last experiment? What would be the result if ammonia were present in place of alcohol? Would phenols behave in a manner analogous to the alcohols?

Compare the results of this experiment with those obtained in Experiment 7.

EXPERIMENT 10

Dissolve 3 drops of acetone in 2 cc. of water. Add $\frac{1}{4}$ cc. of NaOH, and then drop by drop a solution of iodine in potassium

iodide until a pale yellow color remains. When a substance does not respond to this test at room temperature, warm the solution to 60° and, if the iodine color disappears, add a few more drops of iodine solution.

Repeat this experiment, using in place of acetone (*a*) ethyl alcohol, (*b*) methyl alcohol (free from acetone), and (*c*) ethyl acetate.

EXPERIMENT 11

Add a drop of ferric chloride to very dilute (about $\frac{1}{10}$ per cent), aqueous solutions of (*a*) phenol, (*b*) resorcinol, (*c*) acetoacetic ester, (*d*) benzoic acid, (*e*) salicylic acid, and (*f*) *p*-hydroxy benzoic acid.

Some phenols which do not give a typical color with ferric chloride in aqueous solution will do so in alcohol solution. Apply the latter test when the results in water solution are negative.

EXPERIMENT 12

Add bromine water slowly to 5 cc. of dilute (about 1 per cent or less) aqueous phenol solution, until a faint bromine color remains. Repeat the experiment, using (*a*) aniline, (*b*) salicylic acid, (*c*) resorcinol, and (*d*) *p*-nitrophenol.

This test has been used in connection with quantitative determinations of certain phenols. Do you expect phenol ethers and acyl derivatives of aromatic amines to act in the same manner?

Explain why the substituted aniline precipitates instead of remaining in solution as the hydrobromide. Explain why a solution of sodium benzoate may give a precipitate with bromine water in spite of the fact that benzoic acid is only brominated at a fairly high temperature. What inorganic compounds might decolorize bromine with the formation of a precipitate?

EXPERIMENT 13

Heat in dry test-tubes at a temperature of about 140° (using oil or H_2SO_4 bath) for five minutes 0.2 g. of phthalic anhydride with about 0.1 g. of (*a*) phenol, (*b*) resorcinol, and (*c*) α-naphthol, the mixtures having been barely moistened with conc. H_2SO_4.

Add the fusions separately to 10 cc. portions of cold water and neutralize the sulfuric acid with alkali.

Write the formulas for phenolphthalein in acid and in alkaline solution. The production of fluorescein is often applied also as a test for phthalic an-

hydride or phthalic acid. Succinic acid gives a similar color and this is true also of certain other dicarboxylic acids possessing the two carboxyl groups on adjacent C atoms. This test for phenols is not very general.

EXPERIMENT 14

Weigh on the accurate balance about two-tenths of a gram of some organic acid (benzoic may be used). Titrate the sample with standardized KOH solution (approx. N/10) using phenolphthalein as indicator. When dealing with difficultly-soluble acids, a few cubic centimeters of pure alcohol may be used as a solvent.

Calculate the neutral equivalent of the acid according to the formula:

$$\text{Neut. equiv.} = \frac{\text{Wt. of substance} \times 1000}{\text{No. of cc. } N \text{ alkali used}}.$$

Why must phenolphthalein, in preference to methyl orange, be used as an indicator in the above experiment?

The neutral equivalent of an acid is equivalent to the molecular weight divided by the number of acid groups titrated. What is the neutral equivalent of citric acid? When an acid is imperfectly dried, will the neutral equivalent be high or low?

Determination of the neutral eqiuvalent may be applied to most carboxylic acids. The presence of an aromatic amino group will not interfere appreciably in the titrations, but aliphatic amino groups or the presence of two aromatic amino groups will vitiate the results.

Hydroxyl groups and even the presence of a single phenolic group, as in salicylic acid, will not interfere; e.g., ortho- and para-hydroxybenzoic acids possess neutral equivalents corresponding to the molecular weights. In general, the weakly acidic groups, like phenols, amides, and imides, give abnormally high neutral equivalents. What indicator should be selected for the titration of phenol? A strongly acidic phenol like s-tribromophenol may be titrated quantitatively in alcoholic solution using phenolphthalein.

EXPERIMENT 15

Weigh on the horn-pan balance 1.0 g. of benzoic acid and 1.5 g. of PCl_5. Mix the materials in a dry test-tube and after spontaneous reaction has taken place warm the mixture gently so as to dissolve the PCl_5 completely. Pour the solution into 1 : 1 ammonia water and shake the mixture.

This reaction is of considerable value for the preparation of derivatives of many acids. Why is the method not applicable to hydroxy acids and amino acids?

In general, it is advisable to remove the phosphorus oxychloride before

converting the acid chloride into the amide or anilide. This may be done by distillation, (b. pt. 107°) or by the method mentioned in Chapter X, pg. 150.

Acids that are aliphatic in nature, e.g,. butyric acid, cinnamic acid, hydrocinnamic acid, stearic acid, etc., may be converted into the corresponding acyl chlorides by means of PCl_3. In these instances, the acid chloride is relatively insoluble in the by-product obtained and so may usually be separated mechanically. Write the equation for the reaction.

The acid chlorides of hydroxy acids, like salicylic acid, may be prepared by means of thionyl chloride ($SOCl_2$).

PCl_5 may act as a dehydrating agent upon certain organic compounds. It also rearranges oximes into amides (Beckmann rearrangement.)

EXPERIMENT 16

Prepare about 150 cc. of an approximately 1 per cent to 2 per cent acetic or propionic acid solution. Determine the total acidity by pipetting off 10 cc. of the acid solution and titrating against an approximately N/10 NaOH solution. Transfer 100 cc. of the acid solution to a 250 cc. distilling flask and distill two portions of 10 cc. each, titrating them against the same NaOH solution. Express the results of each portion of the distillate in percentage of the total acidity of the 100 cc. used.

The Duclaux values expressed in percentages are as follows:

	Formic	Acetic	Propionic	Butyric	Valeric	Iso-Butyric	Iso-Valeric	Caproic
1. 10 cc.	3.95	6.8	11.9	17.9	24.5	25.0	28.7	33
2. 10 cc.	4.40	7.1	11.7	15.9	20.6	20.9	23.1	24
3. 10 cc.	4.55	7.4	11.3	14.6	17.0	16.0	16.8	19

Why is it unnecessary to use a standardized solution in the above titration?

An approximately N/10 solution is specified for the reason that the titration with 1 or 2 per cent acid solutions will require a convenient volume of alkali for measurement in the burette.

The Duclaux method was proposed for quantitative work but has been found of special value in connection with qualitative identification; e.g., we note the following ratios between formic, acetic, and propionic acids: 4 : 7 : 12, ratios that are very much greater than those between the other physical constants. Moreover, these acids are usually met in aqueous solutions and

the isolation of the anhydrous acids when present in low concentrations is not a convenient operation.

The method is of importance not merely in connection with the identification of the eight compounds listed, but of any compounds that are readily converted into these acids, e.g., the esters, amides, nitrites, salts, etc. It is of course necessary that the total acidity of the solution be due entirely to the volatile acid present and not to inorganic acid.

Outline the method for the identification of propionic acid in the solution obtained by the alkali hydrolysis of propionamide.

ESTERS, ALDEHYDES, AND KETONES

EXPERIMENT 17

Determine the specific gravity at 20° of ethyl benzoate in one of the small specific gravity tubes (cap. about $\frac{3}{4}$ cc.). See page 119, Fig. 10.

Dissolve 2 g. of sodium in 50 cc. of absolute alcohol and add 10 cc. of water after the sodium has dissolved. Withdraw a 10-cc. sample from the homogenous solution for titration against N 4 acid for a determination of alkalinity. Place 40 cc. of the remaining alkaline solution into a 100 cc. r.b. flask and transfer quantitatively from the specific gravity tube the weighed sample of ester. This may be done by means of the capillary tube used for filling the bulb. Small portions of the alcohol from the 40-cc. portion of sodium ethylate solution are used for the purpose of rinsing the tube.

Boil the ester solution under the reflux for one-half hour, cool the contents of the flask, withdraw a 10 cc. portion of the alcoholic solution and titrate the excess alkali against the N/4 acid. From these values the saponification equivalent of the ester may be determined by the use of a formula identical with that used for calculating neutral equivalents of acids.

$$\text{Saponification equivalent} = \frac{\text{Wt. of ester} \times 1000}{\text{No. cc. of } N \text{ alkali used}}.$$

The specific gravity tube is convenient for weighing samples intended for quantitative saponification, since a single trip to the balance serves not only for weighing the sample, but also for an accurate determination of the specific gravity—a constant which may prove of value in connection with the identification of the unknown.

For esters of low molecular weight, the quantity of sodium used must be increased accordingly.

What values for saponification equivalent would be obtained from the following compounds: Ethyl succinate, ethyl acid phthalate, benzaldehyde, diamyl ether?

EXPERIMENT 18

Boil 2 cc. of ethyl benzoate in a small r.b. flask fitted with an efficient reflux condenser, with 30 cc. of 25 per cent NaOH. An ebullator tube will assist in preventing bumping. Saponification will be complete after about thirty minutes, as will be indicated by the disappearance of the ester layer.

A. Examination of the Neutral Saponification Product.—From the alkaline solution, distill about 4 cc. This fraction may be used for the identification of the alcohol in the case of an unknown. Water-soluble alcohols can be salted out with K_2CO_3.

B. Examination of the Acidic Saponification Product.—Cool the residue in the distilling bulb and acidify with *dilute* H_2SO_4. Benzoic acid will separate. Do not mistake a precipitate of sodium sulfate for an organic acid. If in doubt, test the solubility of the product in ether.

When an organic acid is soluble in water, other methods must be used to separate it, viz., (*a*) ether extraction, (*b*) distillation, (*c*) as an insoluble salt. When an ester yields an alcohol insoluble in water, the above indication of completeness of saponification cannot be used.

What kinds of esters yield alcohols that are non-volatile with water-vapor? How will a lactone behave when subjected to saponification?

EXPERIMENT 19

To 1 cc. of acetone add 1 cc. of saturated sodium acid sulfite solution and shake the mixture.

To 10 cc. of a 40 per cent solution of sodium acid sulfite, add $2\frac{1}{2}$ cc. of ethyl alcohol. After several minutes, filter off or pour the clear solution from the small quantity of precipitated salt. This 20 per cent alcoholic solution of sodium acid sulfite is used in the following tests:

To 1 cc. of the sulfite solution, add $\frac{1}{2}$ cc. of acetone. Repeat the experiment, using in place of acetone a $\frac{1}{4}$ cc. portion of (*a*) benzaldehyde, (*b*) heptylaldehyde, and (*c*) acetophenone.

The sulfite addition products of aldehydes and ketones of fairly low molecular weight are quite soluble in water. The progress of the reaction may be nevertheless followed by the generation of heat. Most ketones of high molecular weight do not react but the reaction is quite general for the

aldehydes. When dealing with sparingly soluble aldehydes, particularly with solids, a 0.2 g. sample or such a quantity as will dissolve in ½ cc. of alcohol, may be added to 2 cc. of the sulfite solution. In this instance, the formation of the precipitate may simply be due to the throwing out of the organic compound because of dilution. If the initial compound is soluble in ether, it may easily be differentiated from a sulfite addition product, since the latter will be insoluble in ether.

EXPERIMENT 20

To 1 cc. of *ammoniacal* silver nitrate, add 1 drop of a 5 per cent sodium hydroxide solution. If a precipitate of silver oxide or hydroxide forms, add a drop of ammonia water so as to dissolve it.

Add 2 drops of acetaldehyde solution. Observe whether or not reduction takes place. If the test-tube was previously cleaned with hot NaOH solution, silver is usually deposited in the form of a mirror.

Repeat this test, using in place of acetaldehyde, not more than 2 drops of (*a*) acetone, (*b*) benzaldehyde.

Many compounds, organic and inorganic, in addition to aldehydes, may reduce silver nitrate solution, e.g., the developers used in photography. (Write the formulas for the common compounds used for this purpose.)

What explanation may be given for the failure of the aldehyde group in glucose to react with the reagent? When dealing with water-insoluble compounds ½ cc. of *pure* alcohol may be added.

EXPERIMENT 21

To 2 cc. of fuchsin-aldehyde reagent add 2 drops of acetaldehyde solution. Repeat the experiment, using in place of acetaldehyde 2 drops of (*a*) acetone, (*b*) benzaldehyde, (*c*) formaldehyde solution, and (*d*) acetophenone.

In this experiment, the reagent should not be heated. Why?

To differentiate between formaldehyde and acetaldehyde, add 1 cc. of 25 per cent H_2SO_4 to each of the two test solutions.

The reagent is prepared by dissolving 0.2 g. Fuchsin in 100 cc. of hot water, cooling, adding 2 g. of sodium bisulfite followed by 2 cc. of con. HCl, and diluting to 200 cc.

Water insoluble compounds may be tested in the presence of alcohol (1 cc.) provided that the latter is of sufficient purity so as to give no appreciable color test.

EXPERIMENT 22

A. Water-soluble Aldehydes and Ketones.—Prepare some phenylhydrazine solution by dissolving 1 cc. of liquid phenylhydrazine in 3 cc. of 30 per cent acetic acid. Add ½ cc. of this

solution to a $\frac{1}{4}$-cc. portion of acetone dissolved in 3 cc. of water. Repeat the experiment using $\frac{1}{4}$ cc. of a water-soluble aldehyde in place of acetone.

B. Water-insoluble Aldehydes and Ketones are best tested in the following manner:

Dissolve $\frac{1}{2}$ g. (or less) of the material in a few cubic centimeters (usually 2 cc.) of ordinary alcohol. Now add water, drop by drop, until the precipitate barely redissolves. If by mistake a slight excess of water has been added, a few additional drops of alcohol must be used. To the clear solution, add a quantity of phenylhydrazine equal in weight to that of the unknown being tested. Observe. If the solution remains clear for several minutes, add 1 drop of acetic acid and again observe. Test the following compounds; (*a*) benzaldehyde, (*b*) acetophenone or benzophenone.

Consider the relative advantages of hydrazones, semi-carbazones, and oximes.

The hydrazones, when solid, may be used as derivatives. The method of testing under B usually leads to a product of higher purity. The time required for the precipitation of the hydrazone is of value in predicting something concerning the nature of the compound. The reaction is not very accurate as a time test for the reason that supersaturated solutions may be formed.

A trace of acetic acid catalyses the reaction. Many aldehydes give the test readily, whereas ketones usually require the addition of a drop of acid. This variation may possibly be due to the fact that most aldehydes contain a small quantity of acid as an impurity. The ketones differ among themselves in the time of precipitation.

CARBOHYDRATES

EXPERIMENT 23

A. Fehling's Solution Test.—Dissolve 0.2 g. of glucose in 5 cc. of water. Add 5 cc. of Fehling's Solution and heat the mixture to the boiling-point.

Repeat the experiment using in place of glucose 0.2 g. portions of (*a*) lactose, (*b*) sucrose, (*c*) maltose, and (*d*) glycerol.

Dissolve 0.2 g. of sucrose in 5 cc. of water, add 2 drops of conc. HCl and heat the solution in the steam-bath for five minutes. Neutralize the free acid with alkali and apply the Fehling's Solution test. Sucrose hydrolyzes far more readily than do most polysaccharoses.

B. Osazone Formation.—Into a test-tube place 0.2 g. of a given carbohydrate, 0.4 g. of phenylhydrazine hydrochloride, 0.6 g. of crystallized sodium acetate, and 4 cc. of distilled water. Plug the test-tube with cotton and set it into a beaker of boiling water. Note the time of immersion and the time of precipitation of the osazone. To prevent supersaturation, the tube must be shaken occasionally. Perform this experiment simultaneously with the following carbohydrates: Glucose, sucrose, maltose, and galactose. For time of osazone formation see page 155.

AMINES

EXPERIMENT 24

To a few drops of aniline, add a few drops of acetyl chloride. Pour the reaction mixture into a cubic centimeter of water and note the separation of the acetyl derivative of aniline. Repeat the experiment with a few drops of dimethylaniline, in place of aniline.

EXPERIMENT 25

To $\frac{1}{4}$ cc. of aniline, add 5 cc. of 10 per cent alkali solution and $\frac{1}{3}$ cc. of benzenesulfonyl chloride. Warm the solution slightly. After all the acyl chloride has reacted, cool the solution, filter off any solid material, and acidify the clear filtrate. Agitate the mixture to cause solidification.

How may the benzenesulfonyl chloride test be used to differentiate between primary, secondary, and tertiary amines? (Page 183.)

EXPERIMENT 26

The general method of diazotizating a primary aromatic amine is as follows: Dissolve 1 mole of amine in $2\frac{1}{2}$ moles of hydrochloric acid. Cool to 0°. Add with stirring a conc. solution containing 1.05 moles of $NaNO_2$.

A. Dissolve 1 cc. of aniline in 3 cc. of conc. HCl and add 5 cc. of water. Cool the solution to 0°. Add 0.8 g. of $NaNO_2$ dissolved in 3 cc. of water. Apply the following tests to this solution.

(*a*) Warm 5 cc. of the solution and note the liberation of gas. The latter may be collected over conc. $KMnO_4$ solution to differ-

entiate it from oxides of nitrogen. Does the aqueous solution give a phenol odor?

(*b*) Dissolve 0.1 g. of β-naphthol in 1 cc. of 5 per cent NaOH, and 4 cc. of water. Cool the solution to 10° and add 1½ cc. of the cold diazonium solution.

B. Repeat the first part of the above experiment, using 1 g. of N-monomethyl aniline in place of aniline. Note the separation of the neutral nitroso compound (see page 64).

How may the diazotization of amines be used in qualitative organic analysis to differentiate between various types of amines?

INDIFFERENT GROUPS (CONTAINING NITROGEN)

EXPERIMENT 27

A. Place a few crystals of ammonium benzoate on a watch-glass and add a cubic centimeter of dilute alkali. Note the strong odor of ammonia. Repeat the experiment with (*a*) urea, (*b*) benzamide, (*c*) benzonitrile.

B. Place ¼ g. of urea into a test-tube, add 2 cc. of 20 per cent NaOH solution and boil the solution gently. Is ammonia evolved? Repeat the experiment using in place of urea (*a*) benzamide, (*b*) acetanilide.

What variation is noted in the ease of hydrolysis of various amides? A part of this variation is due to differences in solubility of the organic compound in the aqueous solvent used. The addition of 1 cc. of alcohol will hasten the hydrolysis of water-insoluble compounds.

EXPERIMENT 28

A. To ½ g. of *p*-nitrochlorobenzene, add about 1 g. of granulated tin and add in small portions a few cubic centimeters of 1–1 HCl. Finally, heat the mixture gently. The nitro compound should disappear completely. Pour the reaction mixture into about 10 cc. of water and add enough concentrated NaOH solution to dissolve most of the precipitate of tin hydroxide at first formed and distil a portion of the solution.

The product may be shown to be an amine by its solubility in dilute acid, whereas the original nitro compound was insoluble in dilute acid. Which amines will be non-volatile with water vapor? How may they be separated from the tin-salt solution?

B. Into a small beaker, place 10 g. of iron powder and 5 cc. of water. Add 1 cc. of 5 per cent HCl, and then 1 g. of *p*-nitrotoluene. Stir the mixture with an iron spatula, warming gently to start the reduction. The mixture should be in the form of a paste, but to prevent solidification, $\frac{1}{2}$-cc. portions of water may be added. Finally heat in a water-bath for ten minutes with stirring. The *p*-toluidine may be separated by adding 25 cc. of water and distilling, or it may be separated by extracting the iron paste with 10 cc. of benzene. Note that the product is completely soluble in dilute HCl, thus showing the absence of unchanged nitro compound.

In the above reduction, difficultly-soluble nitro-compounds may react slowly. In such instances, 2 cc. of alcohol may be added with the nitro compound.

When *p*-nitrobenzoic acid is reduced by method B, how may the *p*-amino acid be separated? What precautions must be taken because of the amphoteric nature of the amino acid?

EXPERIMENT 29

Place 1 g. of *p*-bromoacetanilide into a small round-bottom flask and add 15 cc. of a mixture of equal volumes of sulfuric acid and water. Boil under the reflux for one-half hour or until a portion of the liquid on dilution does not give a precipitate of the *original* substance. Dilute the hydrolysis mixture with about 50 cc. of water and precipitate the *p*-bromoaniline by the addition of alkali.

Other reagents for hydrolysis are alcoholic alkali, alcoholic hydrochloric acid, and strong acids under pressure.

Repeat the above experiment with (*a*) acetanilide, and (*b*) benzamide, in place of *p*-bromoacetanilide.

Why does aniline fail to precipitate under the above conditions? How may it be isolated as free aniline? As benzanilide? When benzamide is used, why must the above criterion of completeness of saponification be modified?

EXPERIMENT 30

Dissolve 1 drop of nitrobenzene in 1 cc. of 75 per cent alcohol. Add a drop of NaOH solution and observe any color change. Add a small fragment of 3 per cent sodium amalgam and note any color

changes. Does the amalgam liquefy more readily than in a blank portion containing no nitro compound?

Apply this test to *p*-nitrobenzoic acid and to other nitro compounds. If the unknown gives a very deep color with alkali alone, the amalgam test should not be applied.

Certain nitro compounds in place of reduction to the azo stage under the conditions of the above experiment, form only the light-colored azoxy compounds. In some instances the azoxy derivative will be only sparingly soluble in 75 per cent alcohol, and if so may be used as a derivative. Compounds that dissolve in dilute alkali and which possess groups such as nitro, nitroso, azo, etc., are very readily reduced to the corresponding amino compounds by means of sodium hydrosulfite ($Na_2S_2O_4$) in aqueous solution.

ADD. EXPERIMENTS:

PORTER, 8a (p. 191)
8b (p. 191)
3a (p. 208)

CARBOHYDRATE: NOTES I. 8. Chem. 50 Lab. Sheets.

Diss. 0.1 g. of the subst. in 5 cc. of water, add 2 drops 10% alpha-naphthol in chloroform. Add to 5 cc. conc. sulphuric acid. A red ring between the layers indicates a carbohydrate.

TEST FOR AN ETHER:

Try to diss. liq. in H_2SO_4 – if it does then add ice or cold H_2O & see whether you get a top layer. A top layer will indicate the presence of an ether.

CHAPTER X

THE PREPARATION OF DERIVATIVES

Color reactions, the precipitation of an insoluble compound at a given stage in the analysis, decomposition with certain reagents —reactions that are often used with safety in inorganic analysis as final tests of identification, are applied in organic analysis only as indications. Fortunately, in organic analysis, we may rely more often for final identification upon a variety of physical constants, not only of the unknown, but also of its derivatives. Very often the elementary analysis of an unknown, together with a knowledge of its solubility behavior and its class reactions, will have demonstrated so clearly the type of compound dealt with that the physical constants of the unknown point to but one conclusion. Such a circumstance, however, will seldom justify the failure to prepare a suitable derivative and the identification of the latter by means of its main constants. In this manner, the final possibility of error may be obviated. For special cases, a series of derivatives may be prepared and identified.

THE CHARACTERISTICS OF GOOD DERIVATIVES

1. The compound selected for a derivative should possess physical and chemical properties which will enable an absolute differentiation to be made between the individual possibilities.

2. Solid derivatives are preferable, because of the ease of manipulation of small quantities in preparation and purification, as well as in the determination of constants.

3. The derivative should be prepared by a reaction which gives a good yield of fairly pure product.

4. The derivative should be prepared preferably by a general reaction which under the same conditions would yield a definite derivative with the other individual possibilities. This will eliminate the necessity for a series of specific reactions.

In connection with the application of class reactions, solid derivatives are often obtained which may serve for use in the final identification work. When this is the case, the time required to complete an analysis will be materially lessened.

Occasionally a derivative is met which possesses a melting-point close to that of the unknown; when the product of a reaction melts close to or somewhat lower than the melting-point of the original unknown, the student should question whether or not the original unknown has been recovered, and he should apply additional tests as shown in the following examples:

A. Suppose it is necessary to differentiate between ortho and meta nitrobenzoic acids. Is the amide a suitable derivative?

m-nitrobenzoic acid	m.p. 142°	Amide m.p. 142°
o-nitrobenzoic acid	m.p. 146°	Amide m.p. 176°

In this instance, the amide may serve as a perfectly satisfactory derivative, even though the unknown happens to be the meta compound and the reaction product from amidation melts, let us say, at 140–141°. It will be necessary, however, to demonstrate that amide formation has actually taken place and that the reaction product is no longer soluble in dilute alkali. In addition, mixed melting-points of the original acid with some of the known acid and of the derivative with known *m*-nitrobenzamide will remove all doubt.

B. What derivative, satisfying all (and in particular the fourth) characteristics of a good derivative, can be recommended to differentiate between the four mono-chloro derivatives of toluene?

o-Chlorotoluene b.pt. 159°
m-Chlorotoluene b.pt. 162°
p-Chlorotoluene b.pt. 162°
Benzyl chloride b.pt. 179°

The greater reactivity of the halogen in benzyl chloride will serve, of course, to indicate side-chain halogen. By oxidation with alkaline permanganate, all four individuals yield derivatives, and no special modification of the oxidation method is required for the individual compounds being oxidized. The melting-points of the corresponding acids are 148°, 155°, 240°, and 122°, respectively. The melting-points of the ortho and meta chlorobenzoic acids

(148° and 155°) lie too close together for absolute differentiation. Accordingly, mixed melting-points are resorted to in order to avoid the possibility of error.

THE CHOICE OF DERIVATIVES FOR SOME OF THE COMMONER CLASSES OF COMPOUNDS

In the following discussion, the various types of derivatives that are commonly used are mentioned in approximately the order of their importance in the elementary work of this course. The experimental procedures involved can be outlined in only the most frequently occurring instances and the physical constants of only a limited number of common compounds can be referred to within the limits of the chapter.

Derivatives for Alcohols

1. Solid esters.
   - (*a*) Dinitrobenzoates.
   - (*b*) Benzoates.
   - (*c*) Acetates.
2. Urethanes.
3. Acid phthalates.
4. Oxidation products.
5. Halogen derivatives.

1a. The 3, 5-dinitrobenzoates are convenient derivatives for the water-soluble mono-hydroxy alcohols. Mulliken, I, 168.

In a small test-tube, mix 0.3 g. of 3, 5-dinitrobenzoic acid and 0.4 g. of PCl_5. Warm the mixture slightly to start the reaction and when the rapid reaction subsides, heat the mixture gently for about one minute, when the evolution of HCl should cease. Pour the mixture upon a watch-glass (hood) and after solidification, press the pasty solid upon a clay plate to remove the $POCl_3$. Place the powder into a dry test-tube, add 0.6 cc. of the alcohol, stopper the tube loosely, and warm the reaction mixture on the water-bath during about 10 min. Now add 5 to 10 cc. of water and filter after the product has solidified. Transfer any solid material back to the test-tube and crystallize the ester from about 5 to 10 cc. of ethyl alcohol-water mixture of such strength that the ester will dissolve in the warm solution but will crystallize out on cooling. Dry the material on a porous plate and determine its melting-point.

In actual practice, the above experiment should be carried out by using a known compound side by side with the unknown. The dinitro-benzoyl-chloride is prepared in exactly double quantity, which, after drying, is divided into two equal portions. Thus we may apply the method to a considerable number of alcohols, the dinitrobenzoates of which may not be recorded in the literature. Moreover, material is then at hand for the determination of

mixed melting-points. The latter precaution is especially important, since some of the above melting-points lie rather close to one another and the boiling-points of some of the original material, especially of the higher alcohols, may be lowered by the presence of moisture.

Alcohol	Boiling-point Alcohol	Melting-point 3, 5-Dinitrobenzoate	Melting-point *p*-Nitrobenzoate
Methyl	66°	107°	96°
Ethyl	78°	92°	57°
Propyl	97°	73°	
n-Butyl	116°	64°	
Isobutyl	108°	83°	
β-Chlorethyl	132°	88°	
γ-Chloropropyl	162°	54°	
Benzyl	205°	106°	

Allyl alcohol may be converted into a dinitrobenzoate m. 48°, but it should also be subjected to titration with bromine solution. Isopropyl alcohol may be readily oxidized to acetone by means of chromic acid and the ketone identified by the method given below for acetone.

1b. Benzoates.—A few of the polyhydroxy alcohols (as for example ethylene glycol and glycerol) are readily converted into solid benzoates. In the reaction (Schotten-Baumann) an appreciable excess of benzoyl chloride is used together with sufficient NaOH (10 per cent) to neutralize the acid liberated as well as to decompose the excess acyl halide. The method may be applied also with other acyl halides (*p*-nitrobenzoylchloride, 3, 5-dinitrobenzoylchloride, etc.) which are but slowly decomposed by water.

Alcohol	Boiling-point of Alcohol	Melting-point of Benzoate
Ethylene glycol	197°	70°
Trimethylene glycol	216°	53°
Glycerol	290° d.	72°

1c. Acetates.—Certain high molecular weight alcohols, as well as certain polyhydroxy alcohols, yield solid acetyl derivatives. This type of derivative will be met again among the sugars.

The polyhydroxy-alcohols with four and six hydroxyl groups react with benzaldehyde in hydrochloric acid solution to yield sparingly soluble benzal derivatives, but, unfortunately, such derivatives, as for example, those of erythrite, mannite, dulcite, and sorbite, all melt in the neighborhood of 200°–220°.

2. Urethanes.—The phenyl urethanes are readily prepared by combining phenyl isocyanate with a slight excess [1] of alcohol, warming if the reaction is not spontaneous, and recrystallizing the resultant urethane from a suitable solvent. The diphenyl carbamates are prepared from diphenyl carbamyl chloride $(C_6H_5)_2N \cdot CO \cdot Cl$ but usually a fairly high temperature is required to induce reaction. The phenyl urethanes of methyl, ethyl, propyl, and butyl alcohol all melt within the range of 47° to 61°.

Alcohol	Boiling-point of Alcohol	Melting-point of Alcohol	Melting-point of Phenyl Urethane
Benzyl	204°	....	78°
Phenyl Ethyl	220°	....	79–80°
Cinnamyl	257°	33°	90°
Linalool	198°	....	65°
α-Terpineol	217°	35°	113°
d-Borneol	212°	203–4°	138°

3. Acid Phthalates.—The preparation of acid phthalates and their use for differentiation between primary, secondary, and tertiary alcohols has been discussed in Chapter III. *n*-Butyl and benzyl alcohols, citronellol, geraniol, etc., are conveniently identified by this method.

4. Oxidation Products.—Aromatic alcohols possessing the group $-CH_2OH$ may readily be oxidized to the corresponding acid. Example: Benzoic acid from benzyl alcohol. The method is similar to that to be outlined later in this chapter for the oxidation of side-chains of aromatic hydrocarbons except that the reaction is more rapid and the yields are higher.

5. Halogen Derivatives.—The replacement of the alcoholic –OH group with either bromine or iodine is a typical reaction of alcohols. Since the resulting derivatives are usually liquids, this

[1] Reaction of phenyl isocyanate with water leads to the formation of the water-insoluble diphenylurea.

reaction is used only when considerable amounts of the unknown are available.

Derivatives for Aldehydes and Ketones

1. Aryl hydrazones.
2. Semicarbazones.
3. Oximes.
4. Special condensation products.
5. Oxidation products.

1. Aryl Hydrazones.—The phenylhydrazones of aldehydes and ketones of low molecular weight are generally liquids not adapted for derivatives. By using *p*-bromo-phenylhydrazine, *p*-nitro-phenylhydrazine, or β-naphthylhydrazine, solid derivatives often may be obtained. On the other hand, among the aromatic compounds even the lower members yield solid phenylhydrazones.

	Melting-point of Phenylhydrazone
Furfural	97°
Benzaldehyde	156°
Acetophenone	103°

The method of preparing phenylhydrazones is outlined in Chapter IX, Exp. 22.

2 and 3. Semicarbazones and Oximes.—Semicarbazones and oximes of aldehydes and ketones are generally white crystalline solids, the former being usually the less soluble. Several of the low molecular weight carbonyl compounds, however, yield liquid oximes and it is best to use the semicarbazones for identification of water-soluble carbonyl compounds and the oximes for water-insoluble unknowns.

Preparation of a Semicarbazone.—0.5 cc. of the unknown and 0.5 g. of semicarbazine HCl are dissolved in 5 cc. of water. About 0.7 g. of crystallized sodium acetate is added and the solution set aside for an hour or more in order to permit the semicarbazone to crystallize. The derivative should be recrystallized from a small portion of water.

Preparation of an Oxime.—Oximes of water-soluble carbonyl compounds may be prepared in a manner analogous with that described for the semi-

carbazones, using a hydroxylamine salt in place of the hydrazine derivative. Occasionally the oxime must be isolated by ether extraction. The following procedure is adapted for water-insoluble compounds:

Dissolve 0.5 g. of hydroxylamine hydrochloride in 2–3 cc. of water, add 2 cc. of 10 per cent NaOH solution, 0.2 g. of the unknown, and exactly sufficient alcohol to dissolve the organic compound. The oxime is generally sparingly soluble and may crystallize from the dilute alcohol as it is formed. Often it is best to warm the reaction-mixture on the steam-bath for 10 minutes, using a condenser to avoid loss of solvent. If no sign of reaction is noted after one hour, the mixture is diluted with 2 volumes of water and the precipitated product tested to determine whether it is the oxime or the original unknown. The oximes are usually soluble in dilute alkali and may be reprecipitated by exact neutralization of the alkaline solution. Why is an excess of acid to be avoided?

4. Special Condensation Products.—Several of the most common carbonyl compounds (formaldehyde, acetaldehyde, and acetone) are derivatized best by means of condensation reactions other than those discussed above; the two aldehydes may be condensed with β-naphthol according to the directions outlined by Mulliken, I, pages 23–25.

Methylene-di-β-naphthol, m. 189–92°
Ethylidene-di-β-naphthyloxide, m. 172–3°

The same derivatives can be applied to compounds like methylal and acetal, which may be hydrolyzed to yield the above aldehydes.

Acetone may be condensed (Claisen Reaction) with benzaldehyde under the influence of alkali to yield dibenzylidene acetone,

$$C_6H_5CH{=}CH{-}C(=O){-}CH{=}CH{-}C_6H_5$$

m.p. 111–112°. Three drops of the ketone are dissolved in 2 cc. of alcohol and 0.5 cc. benzaldehyde and 1 cc. dilute alkali added The mixture is heated to boiling for a minute, cooled, and then agitated in order to cause the supercooled oil to solidify. Crystallization from alcohol yields a pure material.

5. Oxidation Products.—Aromatic aldehydes are very readily oxidized to the corresponding acids; some of the members (benzaldehyde, for instance) are readily oxidized even by atmospheric oxygen. A general procedure outlined below for the oxidation of the side-chains of aromatic hydrocarbons is generally applicable to aldehydes also, except that only one-third of the

quantity of permanganate is used. Can this method be recommended for phenolic aldehydes, such as salicyl aldehyde, naphthol-aldehydes, etc.?

CARBOHYDRATES

No great reliance can be placed upon the melting-points of sugars and their derivatives; the values vary with the rate of heating and in the case of the osazones there is too little variation between melting-points of the individual members. It is fortunate, therefore, that an additional, accurately determinable constant is available, namely, the specific rotation. The value for this constant should always be determined in connection with the final identification of a soluble carbohydrate.

Derivatives for Carbohydrates

1. Osazones.
2. Hydrazones.
3. Acetyl derivatives.
4. Mucic acid.
5. Formation of furfural.

1. Osazone formation has been amply illustrated in connection with the classification reactions (see pages 144 and 84). Mulliken gives the following approximate figures for the " Time Test ":

Mannose	$\frac{1}{2}$ min. (ppt. is the hydrazone)
d-Fructose	2 min.
d-Glucose	4–5 min.
l-Xylose	7 min.
l-Arabinose	10 min. (oily)
d-Galactose	15–19 min.
Saccharose (cane sugar)	30 min.
Raffinose	60 min.
Lactose	No ppt. from hot solution
Maltose	No ppt. from hot solution

The crystalline form of the osazones should be compared under the microscope with that of derivatives prepared from known sugars. Which four of the above sugars yield identical osazones, and why?

2. Hydrazones.—For identification by means of melting-points, the hydrazones are of more value than the osazones, but they possess the disadvantage that many of them are soluble in water and therefore isolated with difficulty. The phenylhydrazone of mannose is very sparingly soluble, the corresponding hydrazones of arabinose and galactose are soluble in 50–75 parts of water but not precipitated in such dilutions, whereas those of glucose and fructose are very soluble. A variety of other aryl hydrazones, such as *p*-bromophenylhydrazones, α-methylphenylhydrazones, etc., are also available for the identification of sugars. Cf. Rosenthaler, pages 176–234.

Sugar	Melting-point Phenylhydrazone
Glucose	144–146°
Arabinose	150–153°
Galactose	158–160°
Mannose	195–200°
Fructose	?

3. Acetyl Derivatives.—The acetyl derivatives of sugars may be prepared by the use of acetic anhydride in the presence of a catalyst, such as anhydrous sodium acetate or zinc chloride. Isomeric acetyl derivatives may be obtained, the result depending upon the particular catalyst used. (J. Ind. Eng. Chem. **8**, 380, 1916.)

An Illustration of the Preparation of an Acetyl Derivative.—1 g. of galactose is gently heated with 15 cc. of acetic anhydride in the presence of 1 g. of freshly fused sodium acetate. The solution is heated at the boiling-point for 10 minutes. The acetic anhydride is volatilized by warming on the water-bath (hood), a little alcohol being added to aid in the removal of the anhydride. The residue is washed with cold water to remove sodium acetate and the β-pentacetyl galactose crystallized from alcohol.

	Sodium Acetate	Zinc Chloride
β-pentacetyl galactose	m. p. 142°	α-form 95°
β–pentacetyl glucose	m. p. 132°	α-form 111–112°

For further information, the publications of Hudson should be consulted: J. Am. Chem. Soc. **37**, 1267–1285, 1589–93 (1915).

4. Mucic Acid.—Galactose and its derivatives (lactose, galactosides, etc.), yield the insoluble mucic acid upon oxidation with

nitric acid. A portion of the sugar is slowly evaporated on the water-bath with ten times its weight of nitric acid (sp. gr. 1.15) until a thick syrup is obtained. This is diluted with a little water and allowed to crystallize during one hour. Oxalic acid may also crystallize out but this is readily soluble in warm alcohol. Mucic acid melts at 213°d.

ACIDS

In connection with the identification of organic acids, the neutral equivalents should always be determined. (See page 138.) The volatile aliphatic acids (formic to valeric) should be characterized by means of the Duclaux Constants.

Derivatives for Acids

1. Amides, anilides, and toluidides.
2. Solid esters.
3. Elimination of CO_2.
4. Anhydrides and miscellaneous derivatives.

1. **Amide formation** has already been outlined in connection with the laboratory work, page 138. Low molecular weight acids yield water-soluble amides, and for this reason it is advisable to prepare instead the less soluble anilides or *p*-toluidides (page 144). Mulliken, I, 80–81, has outlined convenient directions for the identification of acetic, propionic, butyric, and isobutyric acids in the form of the corresponding *p*-toluidides. These acids are usually met in aqueous solution and it is not feasible to convert them into acyl halides; instead, the aqueous solution is neutralized with NaOH, evaporated, and the resultant sodium salt utilized in the test.

Preparation of p-Toluidides.—In a dry test-tube, mix 1 g. of *p*-toluidine, 0.4 g. of the powdered sodium salt, and 0.4 cc. of concentrated HCl. Boil the mixture very gently over a very small gas flame during 15 to 30 minutes. Cool, extract the reaction product with 5 cc. of boiling 95 per cent alcohol, pour into 50 cc. of hot water contained in a beaker, and boil down to a volume of about 10 cc. Filter the hot solution through a small filter paper in a heated funnel, crystallize the toluidide from the filtrate, dry, and take its melting-point. Sometimes recrystallization is necessary.

	Melting-point
Acet-*p*-toluidide	146–147°
Propion-*p*-toluidide	123–124°
Isobutyr-*p*-toluidide	104–105°
n-Butyr-*o*-toluidide	72–73°

2. Solid Esters.—A limited number of common acids [1] form solid esters with methyl alcohol; in such instances, the usual esterification process, using 0.5 g. of acid, 3 cc. of methyl alcohol, and $\frac{1}{2}$ cc. of concentrated H_2SO_4 may be applied. After refluxing for 15–30 min., the reaction mixture is poured into 10 cc. of water, the ester filtered off, and recrystallized. Ethyl esters generally melt lower than the methyl derivatives and with increase in molecular weight of the alkyls lower melting-points are observed. (See table on page 151.) With alcohols of fairly high molecular weight, solid esters are again obtained.

Reid has proposed the *p*-nitrobenzyl esters

$$(R\text{–}C(=O)\text{–}O\text{–}CH_2\text{–}C_6H_4\text{–}NO_2)$$

and the phenacyl esters

$$(R\text{–}C(=O)\text{–}O\text{–}CH_2\text{–}C(=O)\text{–}C_6H_5)$$

as convenient derivatives for the identification of hundreds of organic acids.[2]

The *p*-nitrobenzyl esters are prepared by boiling an alcoholic solution of the sodium salt of the organic acid with *p*-nitrobenzyl bromide. For the preparation of phenacyl esters, ω-bromoacetophenone, is used in place of the nitro-benzyl bromide. In the more recent papers in the above series is discussed also the separation and identification of mixtures.

Method.—Dissolve 1 g. of the sodium or potassium salt of the organic acid (accurately neutralize free acids with alkali and evaporate) in a boiling-mixture of 5 cc. water and 10 cc. 95 per cent alcohol. Add 1 g. of *p*-nitrobenzyl bromide and boil the solution during 30 minutes. If an insoluble ester separates from the hot solution, slightly more alcohol may be added. Finally, the solution is cooled, the crystalline ester filtered off, recrystallized from dilute alcohol, and the melting-point taken. Valuable details will be found in the original articles.

3. Elimination of CO_2.—Malonic acid and its homologues readily lose CO_2 when heated to a temperature of about 140–160°. This reaction also takes place at a lower temperature when a solution of the dicarboxylic acid in 20 per cent H_2SO_4 is refluxed. The

[1] *m*- and *p*-Nitrobenzoic acids, the dinitrobenzoic, certain halogenated benzoic acids, terephthalic acid, etc.

[2] J. Am. Chem. Soc. **39**, 124, 304, 701, 1727 (1917); **41**, 75 (1919); **42**, 1043 (1920); **43**, 629 (1921).

resultant monocarboxylic acid may be identified by the methods given above.

Monocarboxylic acids, particularly in the aromatic series, lose CO_2 when heated with soda-lime; in dealing with carboxy derivatives of solid hydrocarbons, this method may prove applicable. For example, the naphthoic acids (α and β) will yield the easily-sublimable naphthalene. In general, synthetical reactions prove superior to analytical reactions for the preparation of derivatives. Why?

4. Miscellaneous.—A variety of common acids may be converted into characteristic derivatives by methods not covered by the above. Details for these less general cases cannot be given here, but a few examples will be cited.

o-Phthalic acid, when heated to its melting-point and maintained at that temperature for a short time, yields the very characteristic, readily-sublimable phthalic anhydride, m.p. 132°.

Cinnamic acid, in common with certain other side-chain unsaturated acids, may be characterized as the dibromide addition product.

Phenolic acids may be identified by reactions involving substitution in the aromatic nucleus. For example, salicylic acid is usually converted into the 5-nitro derivative. Mulliken, I, p. 85.

Acids of the type, $C_6H_4\begin{matrix}CH_2R\\CO_2H\end{matrix}$, may be oxidized by the methods used for side-chain oxidation of aromatic hydrocarbons.

PHENOLS

1. Diphenyl urethanes.
2. Nitration or bromination products.
3. Picrates.
4. Acetyl or benzoyl derivatives.[1]

The acetyl and benzoyl derivatives of many common phenols are liquids or low-melting solids and hence they are suitable for characterization in only a limited number of cases. The diphenyl urethanes prepared with the aid of diphenyl carbamine chloride (see example below) are more generally applicable. Mulliken, I, pages 108–110, outlines directions for nitration of phenol,

[1] For recent work on the dinitrobenzoates of phenols see J. Am. Phar. Assn. **11**, 608 (1922).

phloroglucinol, resorcinol, and thymol; the bromination of phenol and pyrocatechin; and the conversion into picrates of α- and β-naphthols.

Preparation of Diphenyl Urethanes of Phenols.—Dissolve 1 g. of the phenol in 5 cc. of pyridine, add 1 g. of diphenyl carbamine chloride and reflux gently during 30 minutes. The reaction mixture is poured into water. The derivative is filtered off and crystallized from alcohol.

MELTING-POINTS OF DIPHENYL URETHANES

Phenol	104–105°
o-Cresol	72–73°
m-Cresol	100–101°
p-Cresol	93–94°
β-Naphthol	140–141°
Resorcinol	129–130°
Pyrogallol	211–212°
o-Nitrophenol	113–114°

ESTERS AND ANHYDRIDES

Almost invariably, esters are subjected to hydrolysis and the resultant acids and alcohols identified as such or otherwise converted into solid derivatives. When the corresponding amide is characteristic and fairly insoluble, the ester may usually be converted directly into the amide. Quantitative determination of the saponification equivalents are often of value when identifying esters.

Amide Formation.—$\frac{1}{2}$ cc. or 0.5 g. of ester is added to 10 cc. of concentrated ammonia water in a half-ounce bottle, and the suspension observed during several minutes with occasional shaking. If there is no evidence of rapid reaction, the flask is set aside for several hours or until the following day. When working with esters, extremely insoluble in water, a few cc. of alcohol may be added to facilitate reaction. The solid amide is filtered off and crystallized from water or alcohol.

Anhydrides react with ammonia or amines exactly as do the esters except far more rapidly.

AMINES

A. Primary and secondary amines.

1. Acetyl derivatives.
2. Benzoyl derivatives.
3. Benzenesulfonyl derivatives.
4. Phthalyl derivatives.
5. Picrates,[1] chloroplatinates, etc.

[1] For the identification of alkaloid picrates see J. Am. Chem. Soc. **44**, 371 (1922).

B. Tertiary amines.

1. Addition-products with alkyl halides.
2. Substitution products such as nitroso derivatives, (if aromatic in nature).
3. Picrates, chloroplatinates, etc.

The acetyl derivatives are most often used for the preparation of derivatives of primary and secondary amines. Often they may be isolated in connection with the acetyl chloride test for amines (page 144) but usually it is best to prepare them from acetic anhydride. The reaction mixture is poured into water, warmed to decompose the excess of anhydride, cooled, and filtered. The product may be crystallized from water or dilute alcohol.

The benzoyl and benzenesulfonyl derivatives may be prepared in aqueous solution as outlined in Exp. 25, page 144.

The formation of easily characterizable double salts with picric acid, chloroplatinic acid, chloroauric acid, and picrolonic acid is characteristic of many amines, including the tertiary members; these derivatives are of special importance in connection with the identification of quaternary ammonium compounds. The platinum and gold compounds are convenient for quantitative work. (See page 170.)

OTHER NITROGEN COMPOUNDS

The nitrogen-containing groups, other than the amino, that are commonly met are the amide, nitrile, imide, nitro, and azo. As a general procedure, individuals of the first three types are subjected to hydrolysis and those of the last two are converted into reduction products. Definite instructions for these reactions have already been given in connection with the Classification Reactions, page 146, and they will therefore not be repeated here.

In many instances these nitrogen compounds possess other reactive groups and the preparation of a characteristic derivative need not necessarily involve the nitrogen-containing group. For example, *p*-nitrotoluene may be derivatized by reactions involving (*a*) the nitro group, (*b*) the methyl group, and (*c*) the benzene nucleus. In this example, all three types of derivatives will be found to satisfy most of the requirements of good derivatives. Reduction by the procedure described on page 145 yields the volatile *p*-aminotoluene, m.p. 43°, which may be identified as such or converted into the acetyl derivative, m.p. 148°; oxidation of the

methyl group by the alkaline permanganate method described in the following section yields the characteristic *p*-nitrobenzoic acid, m.p. 237°; and nitration according to the methods outlined presently under toluene, yields 2, 4-dinitrotoluene.

In view of the large number of individual compounds, particularly of the mixed type, falling in this section, it seems best in order to conserve the limits of the chapter to consider only a few typical individual examples.

Note and discuss derivatives and methods of preparation selected by Mulliken, Vol. II, for the compounds listed below.

135 Salicyl amide.
168 Phthalamidic acid.
304 Hippuric acid.
1468 Methyl-o-aminobenzoate.
1462 Nitroglycerine.
1568 Diphenylamine.
1733 2, 4, 6-Trinitrotoluene.
1787 Anesthesine.
1946 Antipyrine.
2555 Phthalimide.
2619 Betaine.
2636 Succin-α-naphthalide.
2642 *l*-Tyrosine.
2561 Caffeine.
2651 Theobromine.
2750 Phenyl isocyanate.
2781 Benzonitrile.
2796 Nitrobenzene.
2804 *o*-Nitrotoluene.
2882 Azoxybenzene.
2945 *o*-Nitroaniline.
2989 *p*-Nitrosodiethylaniline.
2996 *p*-Nitrosodimethylaniline.
3016 *m*-Dinitrobenzene.
3027 Benzoyl-*o*-nitroanilide.
3126 2, 4-Dinitrophenol.
3168 Picric acid.
3191 *p*-Nitrosophenol.
36 8-Hydroxyquinoline.
72 *p*-Nitrophenol.
75 *p*-Nitrobenzylcyanide.

139, 164, 425 } Nitrobenzoic acids.

148, 259, 290 } Aminobenzoic acids.

HYDROCARBONS AND THEIR HALOGEN DERIVATIVES

The saturated aliphatic hydrocarbons comprise the class of organic compounds most resistant toward the usual chemical reactions; the preparation of characteristic derivatives is therefore a difficult matter. Moreover, this class of compounds is not ordinarily met in the form of individuals but rather in the form of complex mixtures, as, for example, in the various fractions from petroleum. Final tests applied in the identification of paraffin hydrocarbons, therefore, consist in the application of a variety of physical tests, such as boiling-point range, specific gravity, refractive index, etc. Preliminary work, of course, must conclusively demonstrate the absence of appreciable amounts of compounds other than paraffin hydrocarbons.

In connection with the identification of unsaturated hydrocarbons, valuable data are furnished by titration with bromine; the bromine addition products may often be used for melting-point or boiling-point determinations. Among the terpenes, the addition products formed with bromine, halogen acid (usually HCl), and nitrosylchloride are of considerable value. The latter derivatives react with organic amines to yield nitrosylamines. (Cf. Rosenthaler, pages 22–28.)

	Boiling-point of Terpene	Solid Derivatives of Mono- and Dicyclic Terpenes		
		Melting-point of Hydrochloride	Melting-point of Bromide	Melting-point of Nitrosobenzylamine
d- and *l*-Limonene	175–6°	50°	104°	93°
Dipentene	177–8°			109°
Pinene	155–6°	131°	169–170°	122–3°
Camphene	160°	150–160°		

The halogen derivatives of aliphatic hydrocarbons may usually be conclusively identified by a combination of physical constants accompanied by a quantitative estimation, as outlined in Chapter XI, page 168. A variety of reactions for the preparation of solid derivatives are here available.

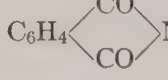
1. Quaternary ammonium compounds.
2. Solid esters.
3. Substituted phthalimides.
4. Reduction products.

1. Quaternary Ammonium Compounds are prepared by mixing one part of the halogen compound with approximately the theoretical proportion of a tertiary amine, such as dimethylaniline, pyridine, quinoline, trimethylamine, etc. The particular tertiary amine chosen should be one yielding a derivative with a convenient melting-point. Occasionally the platinic chloride derivative of the quaternary compound will be found to posses a definite melting-point.

2. Solid esters may be prepared by a method exactly analogous with that given (page 158) for the identification of acids, except that now a salt of a known acid is chosen. The reaction will be found to be less smooth than that involving the use of *p*-nitrobenzyl bromide or phenacyl bromide, since certain halogen compounds may undergo loss of halogen acid with the resultant production of unsaturated compounds; the reaction velocity is also lower.

3. Substituted phthalimides are prepared by heating $\frac{1}{2}$ g. of potassium phthalimide with $\frac{1}{2}$ cc. of a monohalogen compound usually in a sealed tube (150°–200°). The resultant derivatives are insoluble in *dilute* alkali, and thus can be separated readily from unchanged phthalimide.

In the following table are listed a few substituted phthalimides. (Beilstein, II, 1799–1805; II,* 1051–1053.)

Substance	Melting-point
	132°
$-CH_2CH_3$	78–9°
$-CH_2CH_2CH_3$	66°
$-CH(CH_3)_2$	85°

* Supplement of Vol. II.

Substance	Melting-point
$C_6H_4(CO)_2N-CH_2CH_2CH_2CH_3$	65°
$-CH_2CH(CH_3)_2$	93°
$-CH_2-CH=CH_2$	70–71°
$-CH_2-C_6H_5$	115–6°
$-CH_2C_6H_4CH_3$ ortho	148–9°
$-CH_2C_6H_4CH_3$ meta	117–8°

AROMATIC HYDROCARBONS AND THEIR HALOGEN DERIVATIVES

The two main reactions used in connection with the identification of aromatic compounds are (*a*) nitration and (*b*) oxidation of side-chains. Hydrocarbons of the condensed type yield definitely melting picrates.

Nitration.[1]—(*a*) Add ¼ cc. of the unknown to a mixture of 1 cc. concentrated HNO_3 and 1 cc. concentrated H_2SO_4. Agitate the mixture and note any evolution of heat. Finally, warm gently over a small flame and agitate the mixture for at least one minute. After cooling somewhat, pour the reaction mixture upon a small amount of cracked ice. Separate the nitro compound and separate from any oily material by crystallization from alcohol.

Comments: This procedure will yield *m*-dinitrobenzene from either benzene or nitrobenzene, the *p*-nitro derivatives from chlorobenzene, bromobenzene, benzyl chloride, etc. Toluene yields an oily mixture of *o*- and *p*-nitro compounds and should be subjected to procedure (*b*).

(*b*) Add about 3 or 4 drops of the hydrocarbon to 1 cc. of *fuming* nitric acid. Add 1 cc. of 5 per cent fuming sulfuric acid and warm gently over the free flame during about one minute. Isolate and purify the product as under example (*a*).

Comments: Toluene, *o*-nitrotoluene, and *p*-nitrotoluene will yield 2, 4-dinitrotoluene in this reaction; mesitylene, *m*-xylene, *p*-xylene, and pseudocumene yield trinitro derivatives.

Oxidation of Side-chains.—This reaction is applicable to a great variety of aromatic compounds; it is not feasible when the aromatic nucleus contains a phenolic or amino group either of which, when unprotected will lead to the destruction of the ring structure.

[1] *Precaution.*—Even when working with small quantities of material, special precaution must be observed in every nitric acid test, since certain organic substances may react violently. Losses of eyesight may easily result.

Procedure.—Into a 150 cc. r.b. flask,[1] place 75 cc. of water containing 3 g. of $KMnO_4$. Add 1 cc. of the unknown and boil gently under the reflux condenser (why?) for about ¼ to 2 hours, i.e., until the purple color of the permanganate has been replaced entirely by the brown of precipitated manganese dioxide. Filter the mixture and evaporate the filtrate to about one-half volume on the water-bath. Acidify to precipitate the organic acid, recrystallize from water or dilute alcohol, dry, and take melting-point.

Comments: The yield is poor with such hydrocarbons as toluene, ethyl benzene, butyl benzene, etc., but is very satisfactory with the disubstituted products such as the nitrotoluene, the chloro- and bromo-toluenes, the xylenes, etc. When the side-chain consists of a $-CH_2OH$ or $-CHO$ group, the yield will of course be better still and this is true also for the $-CH_2Cl$ and $-CH_2Br$ side-chains. When reactive halogen is known to be present, about ¼ g. Na_2CO_3 should be added to the reaction-mixture.

Compounds with somewhat more complex side-chains may behave somewhat abnormally, for example, acetophenone yields $C_6H_5COCO_2H$ and naphthalene yields some $C_6H_4 \cdot CO_2H \cdot COCO_2H$. In such special cases, the MnO_2 is not filtered from the reaction mixture but the latter is acidified directly. In acid solution, MnO_2 will oxidize quickly the above oxalyl derivatives to benzoic and phthalic acid, respectively. Any excess MnO_2 is then removed by the addition of a little sodium bisulfite.

Preparation of Picrates.—Dissolve 0.1 g. of hydrocarbon (naphthalene, phenanthrene, or acenaphthene) and 0.2 g. of picric acid in 5 c.c. of boiling 95 per cent alcohol. Allow the solution to cool gradually. Filter off the yellow crystals, $RH \cdot C_6H_2(NO_2)_3OH$, and recrystallize from a small amount of alcohol. Dry on a clay plate and take melting-points.

Substance	Melting-point
Picric acid	121°
Naphthalene picrate	150°
Phenanthrene picrate	143°
Acenapthene picrate	161°

[1] A round-bottom flask is required since bumping may break an ordinary flask. A copper utensil avoids the difficulty of "bumping."

CHAPTER XI

QUANTITATIVE ANALYSIS OF SUBSTITUENT GROUPS

It will seldom be necessary in this course to resort to methods of ultimate analysis, and it is for this reason that combustion methods for carbon, hydrogen, and nitrogen are omitted from this chapter. This is true also of the Carius determination for halogens and the fusion methods for sulfur, arsenic, and phosphorus. In dealing with compounds of unusual difficulty, the methods of ultimate analysis may have to be employed, but under such circumstances the student is directed to other sources [1] where directions will be found in more detail than would be justifiable here.

Several of the qualitative methods and particularly the estimation of certain reactive groups, however, are of considerable value in connection with identification work, not merely in the first stages of an analysis but also in connection with confirmatory tests when the preparation of derivatives is not feasible. Moreover, a considerable number of such tests involve simple volumetric methods and require comparatively little time when the standardized solutions are available. Some of the more adaptable methods are, therefore, given here but the student is encouraged to become familiar with more advanced treatments of the subject [2] that will supply a greater variety of methods together with valuable references to the original articles.

Determination of Nitrogen by the Kjeldahl Method.—Most organic compounds in which nitrogen is present in non-oxidized form are decomposed when digested with sulfuric acid with the resultant formation of ammonium sulfate. The ammonia may

[1] Weyl, Meyer, Lassar-Cohn, etc. Some of the more elementary laboratory manuals give excellent treatments of the subject. This is true especially of Gattermann's Practical Organic Chemistry, Noyes' Organic Chemistry for the Laboratory, and Fisher's Laboratory Manual of Organic Chemistry.

[2] For references, see the end of this chapter.

then be liberated with a non-volatile alkali, distilled from the mixture into a known volume of standard acid, and determined volumetrically by titrating the excess acid.

A known weight (usually 0.300 g.) of the substance is placed in a 500 cc. Kjeldahl flask and dissolved in 25 cc. of pure concentrated sulfuric acid. Five grams of potassium sulfate and 0.25 g. of copper sulfate are added and the mixture gradually heated to boiling over a small flame and subsequently digested at the boiling temperature during one or two hours or until the liquid is practically colorless.

The oxidized mixture is allowed to cool, diluted carefully with 250 cc. of distilled water and a few chips of porous plate added. A 40 g. portion of solid stick NaOH c.p. is then carefully added to the cool solution and the flask immediately connected with the condensing apparatus, the receiving flask of which must be in place. After the caustic has dissolved, the solution is slowly distilled until at least 100 cc. of distillate has been collected. This should require about one-half hour.

The receiving flask consists of a 250-cc. Erlenmeyer flask containing 30 cc. of standard 0.2 N. sulfuric acid and a few drops of congo red (or methyl orange) indicator. The tip of the exit tube should be immersed in the standard acid. After the distillation is complete, the excess acid is titrated with 0.2 N alkali.

Since some of the materials used in the analysis will contain traces of nitrogenous matter, it is necessary to run a blank determination and apply the correction to the values obtained with the unknown.

The results are calculated either as percentage of nitrogen or according to the formula:

$$\text{Equivalent Weight}^{1} = \frac{\text{Wt. of Sample} \times 1000}{\text{Cc. Normal acid used}}.$$

DETERMINATION OF HALOGENS[2]

Most organic halogen compounds including many of the more stable aromatic types are readily decomposed by metallic sodium in absolute alcohol. The halogen is then precipitated by the addition of standard $AgNO_3$ solution and the excess of the latter determined by titration according to the Volhard method.

A known weight of the organic compound (about 0.250 g.[3]) is placed in

[1] This value will be equal to the formula weight if the molecule contains one nitrogen atom; when two or three nitrogens are present, the apparent molar weight will be one-half or one-third, respectively, of the actual molar weight.

[2] Stepanow, Ber. **39**, 4056 (1906). Noyes Lab. Manual, 1916, p. 23.

[3] If the substance is a liquid, the portion used in the specific gravity determination is utilized and therefore no additional weighing of sample is required.

a 100-cc. long-neck r.b. flask together with 35 cc. of absolute alcohol. The solution is heated to boiling under a condenser and 3.5 g. of metallic sodium added gradually to the boiling solution during about twenty minutes. Finally, the solution is heated for one-half hour longer, when the sodium should be dissolved.

Cool the solution and add *cautiously*, through the condenser, 50 cc. of distilled water. Transfer the solution to a 250 cc. Erlenmeyer flask, acidify with nitric acid (chlorine-free), filter if necessary, and precipitate the silver halide by the addition of a slight excess of N/10 $AgNO_3$. Add ferric alum as an indicator and titrate the excess $AgNO_3$ by means of N/20 thiocyanate solution. (If the halide is chlorine, the ppt. of AgCl should be filtered off before titrating with thiocyanate. Why?)

In the calculation of results, use a formula analogous with that given above under the nitrogen determination.

Ionizable Halogen.—Substances yielding ionizable halogen when dissolved in water can usually be estimated directly without the digestion with sodium. The most common substances met in this class are the hydrochlorides of organic bases.

ANALYSIS OF METALLIC DERIVATIVES

Na, K, Ca, and Ba Salts.—About a 0.250 g. portion of the sample is weighed out in a tared platinum[1] or porcelain crucible and heated in a drying oven at 120° for several hours, until constant weight is attained. The loss in weight usually represents water of crystallization. Occasionally, substances are met that require drying at appreciably higher temperatures.

The crucible is now heated over a small free flame until all initial decomposition is complete. After cooling, the residue is treated with two drops of concentrated sulfuric acid, heated very gently with indirect flame until fumes of SO_3 cease to escape, and finally heated to dull redness until the residual sulfate is practically white. (With sodium and potassium sulfates, the heating must be sufficiently low to prevent volatility.) The residual sulfate, that may be contaminated with a trace of sulfide, is best treated with one more drop of H_2SO_4, and heated to constant weight.

Ammonium Salts.—Ammonium salts may be estimated by the Kjeldahl procedure without requiring sulfuric acid digestion.

[1] Platinum is not used in the presence of phosphorus, arsenic, lead, etc. Why?

Silver and Platinum Salts.—In connection with identification work, silver salts of organic acids and platinic chloride double salts of organic bases are prepared, particularly when only small amounts of material are available for investigation. The silver salts are prepared by exactly neutralizing the organic acid with NaOH, adding the requisite amount of silver nitrate, filtering, washing thoroughly with water, and drying at 100°. The platinic chlorides are prepared by dissolving the organic base in hydrochloric acid, adding about $\frac{1}{2}$ mole of chloroplatinic acid, filtering off the salt, $(R\text{–}NH_3)_2PtCl_6$, and crystallizing from alcohol when feasible.

A 0.200 g. portion of the dry salt is then gently ignited in a porcelain crucible and weighed either as metallic Ag or as metallic Pt.

In addition to being of constant composition, the platinic chlorides of some organic bases possess definite melting-points and characteristic crystalline structures. The latter property, especially, suggests their importance in micro-analysis.

ESTIMATION OF UNSATURATION

A number of the simple ethylene derivatives may be titrated quantitatively with bromine. The test is, of course, applied only when the previous classification reaction has shown that bromine is decolorized without appreciable substitution taking place. The weighed substance (about 1 g.) is dissolved in 25 cc. of carbon tetrachloride, the mixture cooled in a freezing bath, and titrated with a bromine solution of known strength (about N/2) until a faint bromine color remains.

The following modified method, that of Hanus, is of general application and serves also in technical analysis for the determination of the iodine numbers of natural products such as fats, fatty acids, waxes, etc.

The iodine solution is prepared by dissolving 13 g. of iodine in 1000 cc. of glacial acetic acid and adding 3 cc. of bromine to the cold acetic acid solution.

A 0.200 g. sample is transferred to a 250 cc. glass-stoppered Erlenmeyer flask and dissolved in 10 cc. of chloroform. To this solution there is now added 25 to 50 cc. of the iodine solution (about 50 per cent excess should be used), and the mixture allowed to stand, with occasional shaking, for thirty minutes.

The reaction mixture is next treated with 2 g. of KI dissolved in about 10 cc. of water, shaken thoroughly, and 100 cc. of distilled water added. The

excess of iodine is titrated with standardized N/10 sodium thiosulfate solution until only a faint iodine color remains. The solution is now again shaken. One cc. of starch paste is added, and the titration continued until the blue color just disappears.

While the above determination is being carried out, a blank determination is conducted in exactly the same manner. This is essential because changes in the acetic acid-iodine solution make it inadvisable to assign a definite normality factor to this solution.

The iodine number of a substance represents the percentage of iodine (or its equivalent) absorbed by the sample. Thus when a sample weighing 0.200 g. absorbs an equal weight of iodine, it possesses an iodine number of 100.

ESTIMATION OF HYDROXYL

The hydroxyl group is estimated best by indirect methods. The hydroxyl compound is converted into an acetyl, benzoyl, or analogous derivative and the resultant ester subjected to saponification according to the method described below for esters. The molar equivalent of the hydroxy compound is thus equal to the saponification equivalent of the ester minus the molecular weight of the acyl radical with a +1 correction for the hydrogen atom. In this determination, it is, of course, also essential to subject the original compound to saponification test. For example, the compound $\begin{matrix}\text{CHOH}\text{–}\text{CO}_2\text{C}_2\text{H}_5\\ |\\ \text{CHOH}\text{–}\text{CO}_2\text{C}_2\text{H}_5\end{matrix}$ will yield the corresponding diacetyl derivative but upon saponification of the latter, four molecules of alkali will be involved.

The reaction products of certain alcohols with phthalic anhydride, $\text{C}_6\text{H}_4\begin{matrix}\text{CO}_2\text{R}\\ \diagup\\ \diagdown\\ \text{CO}_2\text{H}\end{matrix}$, may be isolated and used for the determination of neutral equivalents. The molar weight of the radical R may thus be determined.

ESTIMATION OF THE CARBONYL GROUP

This determination is seldom required and consequently no detailed directions are given. The references at the end of this chapter should be consulted. The main methods are as follows:

1. By choosing a hydrazine derivative of sufficiently high molecular weight, like β-naphthylhydrazine, extremely insoluble,

solid hydrazones are obtained and these may be weighed directly after drying in the oven.

2. The carbonyl compound in alcohol is treated with a slight excess of hydroxylamine sulfate solution. A known amount, but no excess, of standardized alkali is now added. After completion of the reaction, the remaining hydroxylamine is titrated with standard acid using methyl orange.

3. The aldehyde or ketone may be converted into the phenylhydrazone and the excess of reagent determined by measuring the volume of nitrogen gas liberated by Fehling's solution at the boiling temperature. The hydrazone is not attacked by this oxidizing agent.

$$C_6H_5NHNH_2+O \rightarrow C_6H_6+N_2+H_2O$$

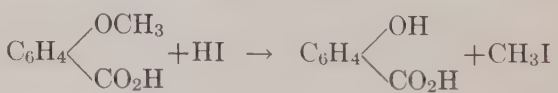
4. Important quantitative methods in the sugar group are based upon the behavior of reducing sugars with Fehling's solution. The amount of reduction that has taken place, under certain specified experimental conditions, may be determined from the amount of Cu_2O formed, which may be estimated either gravimetrically or volumetrically. In connection with identification of individual sugars, this method is however of little value.

ESTIMATION OF THE CARBOXYL AND ESTER GROUPS

The carboxyl group may be determined by direct titration according to the method suggested in the classification reactions in Chapter IX, Exp. 14. The saponification of esters, likewise, is illustrated in laboratory experiment No. 17.

ESTIMATION OF ALKOXYL GROUPS

The Zeisel method [1] is based upon the fact that alkoxyl groups, whether in ethers or esters, are decomposed by heating with strong hydriodic acid to yield alkyl iodides. The latter are absorbed in alcoholic $AgNO_3$ and estimated as AgI.



[1] Internat. Cong. Applied Chem. III, Vol. 2, p. 63 (1898). J. Chem. Soc. **81,** 318; **115,** 193 (1919).

When the Zeisel method is applied to compounds containing nitrogen, it must be remembered that alkyl groups on nitrogen may occasionally be partially replaced to yield alkyl iodides. On the other hand, under the influence of HI, an alkyl group might conceivably be transferred from oxygen to nitrogen.

The apparatus ordinarily used in that shown in Fig. 12.

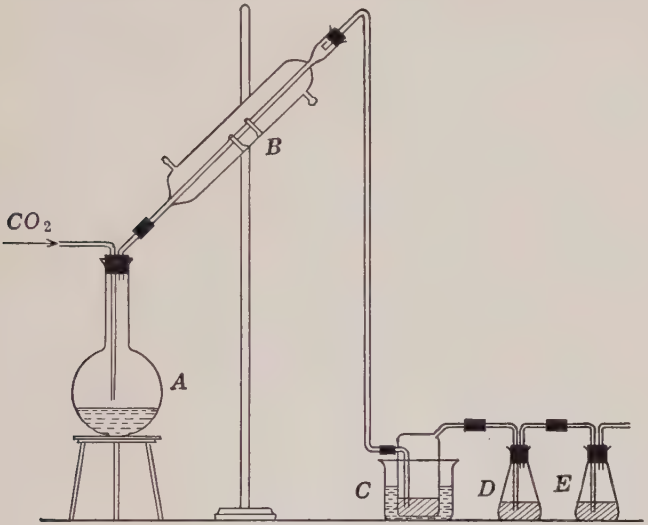


FIG. 12.

For the analysis of a 0.300 g. sample, the 50 cc. r.b. flask *A* is charged with 15 cc. of redistilled aqueous hydriodic acid (sp. g. 1.68), a chip of clay-plate and a trace of red phosphorus. It is connected with the small condenser *B* containing water at about 40–60° which, in turn, is connected with three wash bottles *C*, *D*, and *E*. The first contains warm water and ½ g. of red phosphorus to remove HI and I_2 vapors, while *D* and *E* contain 40 cc. and 20 cc. respectively of a saturated solution of $AgNO_3$ in absolute alcohol.

Before proceeding with an analysis, a blank test is made. The flask *A* is heated to cause appreciable refluxing. A stream of CO_2, purified by passing through aqueous $AgNO_3$ and next through H_2SO_4, is passed through the apparatus (but not through the HI solution) as indicated. No turbidity should be observed in the flask *D* during an interval of about 10 minutes.

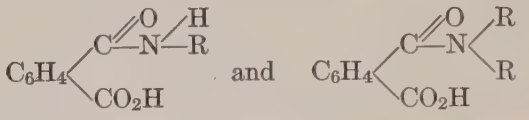
The flask *A* is now cooled, the sample introduced, and the heating and passing of CO_2 repeated. A white precipitate of the silver iodide-silver nitrate double salt separates in flask *D* after about 10 minutes and the reaction is usually completed in 40 minutes.

The silver nitrate solutions are now combined, diluted with several volumes of water, acidified with nitric acid, boiled gently for several minutes, and the silver iodide determined gravimetrically.

The above procedure is satisfactory with non-volatile unknowns. In dealing with appreciable volatile products, special precautions must be taken in adding the weighed sample and the water in the condenser B must be kept cold during the early stage of the heating.

ESTIMATION OF THE AMINE GROUP

1. The derivatives formed by the reaction of primary and secondary amines with phthalic anhydride,



may be isolated, purified by crystallization from water or dilute alcohol, dried, and titrated against standard NaOH as in the determination of neutral equivalents of other organic acids. By subtracting 148 from the neutral equivalent value, the equivalent weight of the amine is obtained. A modification of this method is outlined below.

2. Many free aliphatic amines may be titrated directly with standard acid in the presence of methyl orange or congo red. Salts of weak bases (*aryl* amines) with strong inorganic acids (HCl, H_2SO_4, HNO_3) may be titrated directly with standard alkali using phenolphthalein as an indicator.

The above phthalic anhydride method for the estimation of the primary and secondary amine groups may be modified as follows:

0.200 g. of pure phthalic anhydride [1] is placed in a dry 100 cc. glass-stoppered cylinder and dissolved in about 5 cc. of benzene. To this solution there is now added 0.100 g. of the amine under examination dissolved in 10 cc. of benzene or alcohol-free ether. The mixture is thoroughly shaken during several minutes. 27.0 cc. of N/10 NaOH is added and the solution again shaken for several minutes in order to insure decomposition of any excess of phthalic anhydride. A few drops of phenolphthalein are now added and the solution titrated to the neutral point with N/10 acid. Since 27 c.c. of N/10 alkali represents the exact amount required for neutralization of the phthalic anhydride, the amount of N/10 acid consumed serves for the calculation of the equivalent weight of the amine.

$$\text{Equivalent Weight} = \frac{\text{Wt. of sample} \times 1000}{\text{Cc. N/1 acid used}}$$

[1] With amines of low m. wt. (below 74), the amount of phthalic anhydride must be increased and a proportional volume of alkali used.

The above test possesses distinct advantages over the older acetic anhydride method. Phthalic anhydride is obtainable in practically 100 per cent purity and blank determinations are usually not required. Moreover, since the reagent is a solid, it may be weighed more conveniently. The method may experience a limitation in a few special instances where insoluble salts are formed between the organic acid and the amine; in such instances the alkali must be added slowly and in small portions so as to liberate the amine and permit complete reaction with the anhydride.

REFERENCES

Meyer: Analyse und Konstitutionermittelung organischer Verbindungen.
Weyl: Methoden der organischen Chemie.
Allen: Commercial Analysis.
Sherman: Organic Analysis.
Lassar-Cohn: Arbeits-Methoden.
Meyer-Tingle: Determination of Radicals in Carbon Compounds.
Vaubel: Methoden der quantitativen Bestimmung organischer Verbindungen.
Kingscott and Knight: Methods of Quantitative Organic Analysis.

CHAPTER XII

EXAMINATION OF MIXTURES

THE ideal method to be followed in the identification of the components of a mixture consists in, first, separating the unknown into its pure individuals and, second, identifying each individual according to the method already outlined (Chapter VI). Only in exceptional instances will it be permissible to attempt an identification of the constituent of a mixture without a previous separation.

The laboratory work in this part of the course will include a study of two or three relatively simple mixtures, each consisting of from two to six components. The identification of these mixtures will require a thorough mastery of the preceding work, especially since it is impossible to outline a set of procedures that may be applied directly to the great variety of combinations that may be met. More or less specific instructions may be given, however, concerning the preliminary examination of mixtures.

A thorough preliminary examination should always precede any attempt made to separate a mixture.—To the experienced analyst, certain " short-cuts " will always be apparent, but for the beginner and usually for the experienced chemist also, a thorough preliminary examination is by far the best " short-cut " to be found. In the case of a liquid unknown, there is always the temptation to proceed immediately to a fractional distillation and in the case of a solid mixture we find too often that the first attempt at analysis has been a resort to the use of the wrong solvents. It is only after the preliminary examination that one can decide upon the most logical and satisfactory method for the final separation. Although these preliminary tests are usually similar for different mixtures, the final methods of separation will be different in every case, since it will then be possible to dispense with all unnecessary steps.

In outlining methods for the preliminary examination, we shall limit ourselves to two types of mixtures: (*a*) water-insoluble and (*b*) water-soluble. Naturally, many mixtures will fall in an intermediate field, some of the ingredients being water-soluble and others insoluble in water. Alcoholic solutions of water-insoluble compounds furnish a very common example of this type. Frequently the solubility in water of certain ingredients will be appreciably affected by the presence of other compounds, particularly by solvents. It is felt, however, that a study of the common methods of attack of the two extremes will enable the student to deal effectively with intermediate types also. Occasionally, it may be necessary to conduct preliminary examinations on both the water-soluble and the water-insoluble parts of a mixture; such examinations are not conducted independently but the results found in the examination of one fraction are used to facilitate the study of the other.

The greatest possibility of error in connection with the separation of mixtures lies in missing an ingredient which, although of importance, may be present only in traces and may require some special test. In actual technical work, such difficulties are only apparent since additional information concerning the source of the material and the use for which it is intended is usually available.

In connection with a study of mixtures, it is essential to keep in mind continually the possibility of interaction between the ingredients and especially the possibility of decomposition during the process of separation; for example, easily hydrolyzable esters, amides, and anhydrides may be met in the form of their decomposition products. Cases of doubt call for a study of the original sample.

OUTLINE FOR THE PRELIMINARY EXAMINATION OF A MIXTURE

(Record notes in the order outlined here)

Mixtures of Type A. (Insoluble in Water.)

I. Physical Characteristics.—Examine the unknown for color, odor, homogeneity, etc. In the case of a solid, it will often be possible to observe various forms of crystals (and especially so when a microscope is used) and often small fragments of the pure

individuals may be isolated mechanically. If this is possible, it is, however, no excuse for a variation in the following steps, since a more effective method of separation will usually be found. In the case of certain mixtures, as when a solid is in suspension in a liquid, or when dealing with two liquid layers, it is best to separate the mixture into two parts, filtering in the first instance and using the separatory funnel in the second. Tests should then be made upon each portion of the mixture. In such cases, it is to be expected that certain ingredients will be found in both parts of the mixture.

II. Ignition Test.—Ignite a small amount of material on platinum foil or in a crucible and apply the usual observations, viz., fusion temperature, appearance of the flame, odor, presence of inorganic material, etc.

III. Elementary Analysis.—Although analyses will be made on the fractions to be separated later, it is necessary to run also an elementary analysis on the original mixture; the result obtained may serve to detect an ingredient which might otherwise be overlooked.

IV. Solubility Behavior.—The solubility tests differ from those applied to individual compounds in one essential point; it is necessary to determine whether any part of the mixture has dissolved. This is done by separating the solvent and examining it for dissolved material by precipitation, extraction, or distillation methods, or by combinations of such methods. Diminution of volume in liquid unknowns is occasionally of value. The following scheme is of value in connection with the application of solubility tests on a *water-insoluble* mixture. A one-gram sample will usually serve for these tests and the suction pipette, page 112, will be found of particular value in connection with the separations and extractions. All fractions are to be retained for later use.

Fraction C will contain the water-insoluble basic compounds as well as amphoteric compounds; alkalinization will precipitate the former but not the latter. From fraction D the insoluble acids may be removed by acidification. How will you test for the amphoteric group?

In order to secure reasonably sharp separations, it is well to apply two acid and alkaline extractions respectively. It is well also to wash fractions C and D with small portions of ether (Why?), although these ether washings may be discarded. Before precip-

itating the organic bases and acids from fractions C and D, it is advisable to remove dissolved ether (Why?) by gentle warming.

UNKNOWN. If Liquid, Remove any Volatile Solvent by Distillation on Water-bath

Volatile Solvent A	Residue. Treat with Ether		
	Insoluble Part B	Soluble in Ether. Treat with dilute HCl.	
		Soluble Part C	Ether Layer. Wash with a small volume of H_2O. Treat with dilute KOH.
			Soluble Part D
			Ether Layer. Dry with a little Na_2SO_4 and evaporate to obtain indifferent compounds. E

V. Subsequent Fractionation.—The various fractions obtained in connection with the solubility tests will not necessarily consist of individual compounds; each fraction may require further separation, for example, D may consist of a mixture of acidic compounds and E of a mixture of neutral substances. Tests for homogeneity must therefore be applied to the individual fractions and, if necessary, a given fraction must be subjected to further separation. This is done usually in connection with the final separation of the main mixture. Suggested procedures will be discussed subsequently and are also illustrated in the problems at the end of this chapter.

VI. Outline of Plan.—Using the data obtained above, record in your notebook a list of possible homologous series present in the mixture and outline in your notebook a diagrammatic scheme for the separation of the mixture, submitting this to your instructor for his approval.

VII. Proceed with the Final Separation of the Mixture.—Use a weighed quantity of material and weigh the separate fractions obtained.

VIII. Identify the individuals isolated from the mixture by the steps previously outlined (Chapter VI) for the Identification of Individual Compounds.

Mixtures of Type B (Water-soluble)

I. Preliminary examination as described under Procedure A.

II. Ignition Test.—Ignite a small amount of the material on platinum foil. If the substance does not burn readily, it may be an aqueous solution and whether or not this is the case will be indicated by the fact that the mixture is soluble in water but insoluble in ether and possesses a low boiling-point.

III. Elementary Analysis.—Precaution! Do not apply the sodium decomposition test to aqueous solutions! In such cases, reserve the elementary analysis until the individual fractions are being examined. The aqueous solution should be examined, however, for inorganic radicals.

IV. Solubility Behavior.—Apply the following tests to the aqueous solution:

(*a*) Test aqueous solution with litmus and phenolphthalein.

(*b*) Extract a small portion with ether, dry the latter with anhydrous Na_2SO_4 and evaporate on a watch glass, avoiding condensation of moisture.

(*c*) To a small portion, add HCl (unless the original is strongly acidic) and cool. Note evolution of gas, formation of precipitate, etc. Apply an ether extraction test to the acidified solution.

(*d*) To a small portion, add KOH and cool. Observe color changes, evolution of gases, formation of precipitates, etc. Apply an ether extraction test to the alkaline solution.

(*e*) Evaporate a cubic centimeter of the original aqueous solution to dryness on the water-bath. Is a residue left?

V. Distillation and Miscellaneous Tests.—Aqueous solutions should be subjected to the following distillation tests. This method of separation is particularly valuable in the examination of quite dilute (1 to 5 per cent) aqueous solutions. Any individual volatile fraction may be further concentrated by redistillation.

(*a*) To a portion of the original mixture, add NaOH and distill *carefully*.

Volatile Part	Non-volatile part. Add dilute H_2SO_4. Distill. If sulfuric acid causes charring, use phosphoric acid.	
Aqueous solution of: Volatile Bases Volatile indifferents Alcohols Aldehydes Ketones If the sp. gr. of this distillate is that of pure water then this group is absent. How would the basic group be separated here from the indifferent?	Volatile Part Volatile acids If distillate is neutral or requires only a little N/10 alkali for neut. then volatile acids are absent.	Non-volatile part Contains K_2SO_4 with non-volatile part. This non-vol. part may be different from that obtained by evaporation of the original solution. Why?

From the aqueous solution containing only the volatile indifferents, the latter may be salted out very effectively with K_2CO_3 unless the solution is too dilute.

(*b*) Apply the phenylhydrazine test, the iodoform test, the $FeCl_3$ test, the Br_2 water test, etc., to small diluted portions of the original solution, or, better still, to the volatile part of the mixture. Be sure that these tests are applied under proper conditions, especially when applied to the original mixture. To illustrate: Sulfates or oxalates might yield precipitates with phenylhydrazine, sulfites would decolorize Br_2 water, etc.

VI, VII, and VIII. (Proceed as Outlined for Mixtures of Type A.)

After a mixture has been separated into certain groups (acidic group, indifferent group, etc.), it is necessary to determine by the application of the usual tests for purity whether these fractions consist of one or several individual compounds.

When more than one individual is found in a given solubility group, additional operations are involved; subsequent separations are effected preferably by physical methods but, as a last resort, chemical methods which yield certain products in the form of derivatives may be required.

Physical methods of separating a given solubility fraction consist in the application of fractional distillation, fractional crystallization, crystallization from solvents of various types, steam distillation, sublimation, etc. Such operations are already familiar to the student but nevertheless abundant opportunity remains for the exercise of his ingenuity when relatively small amounts of material are available.

Separation of the Acidic Fraction

Among the acidic substances, separations may be effected occasionally by taking advantage of the variations in acidity. When excess carbon dioxide is passed into the solution of the acidic fraction in alkali, weak acids (when sparingly soluble in water), as, for example, certain amides, imides, phenols, etc., will be precipitated while the stronger acids remain in solution.

The principle of fractional precipitation is often of value when mere crystallization fails. The fraction is dissolved in alkali (dilute solution) and precipitated in fractions by the cautious addition of dilute hydrochloric acid. In working with sparingly soluble acids, the solutions must be dilute and the acid added with vigorous stirring in order to prevent the contamination of the product with salts of the organic acids.

The use of insoluble salts (calcium, lead, etc.) may occasionally be used to advantage in the separation of mixtures of carboxylic acids.

Among the volatile fatty acids, the Duclaux method is applicable not merely to identify the individual compounds but also to examine mixtures. An aqueous solution containing the volatile acidic fraction is distilled and the distillate collected in three fractions. If the first and third fraction, after dilution and determination of the Duclaux values, yield checking results, proof is at hand that only one individual is present. If the first and third fractions differ considerably in the Duclaux values, a mixture is indicated. The results sometimes serve to identify the individual acids.

Separation of the Amine Fraction

The basic compounds, if solid, are subjected to crystallization and occasionally to fractional distillation; in this group, steam

distillation may aid in effecting a separation. Fractional crystallization of certain salts of the amines is also of value; for this purpose the sulfates are utilizable but for special work the platinic chloride double salts are adaptable.

It is often important to separate the three classes of amines, and this may be done by the application of the benzene sulfonyl chloride reaction. Cf. page 144.

Mixture of Amines.

Add aqueous KOH and $C_6H_5SO_2Cl$. After completion of reaction, filter or extract with ether.

<table>
<tr><td>Soluble in aqueous layer:
Salt of sulfonyl derivative of prim. amine. Acidify to precipitate derivative of prim. amine.</td><td colspan="3">Ether layer:
Tert. amine, sulfonyl derivative of sec. amine and some disulfonyl derivative of prim. Treat ether solution with dilute HCl.</td></tr>
<tr><td></td><td>Soluble in HCl:
tert. amine as hydrochloride.</td><td colspan="2">Soluble in ether layer:
Sulfonyl derivative of sec. amine and disulfonyl derivative. Evaporate ether and warm with alcoholic KOH to decompose disulfonyl derivative. Dilute with water.</td></tr>
<tr><td></td><td></td><td>Soluble:
Derivative of prim. amine.</td><td>Insoluble:
Derivative of sec. amine.</td></tr>
</table>

A separation similar to the above can be based upon the reaction of the amines with phthalic anhydride, cf. page 62. A more common procedure consists in the treatment of the amine fraction with acetic anhydride, the separation of the tertiary amines by means of dilute acid and separation of the acetyl derivatives of the remaining members by crystallization.

Separation of the Indifferent Fraction

In work with the indifferent compounds, the physical methods already enumerated are generally of primary importance. Chemical reactions are also available. For example, a mixture boiling

at a fairly constant temperature (140–145°) consisted of a hydrocarbon and an ester; the latter was saponified and identified by the hydrolysis products and the hydrocarbon recovered as a pure individual.

Cold concentrated sulfuric acid may serve often for the separation of saturated hydrocarbons from their oxygenated derivatives. This reagent can be employed only when no decomposition of the dissolved material is observed.

Dimethyl sulfate, used in connection with the classification reactions, may be utilized also for the separation of aromatic from saturated aliphatic hydrocarbons. Several treatments may be required to secure a complete separation. The aromatic hydrocarbon may be recovered from the dimethyl sulfate after saponification of the latter. (Precautions, see page 135.)

Mixtures Compounded by Nature

Many mixtures met in technical work, particularly when from natural sources, are exceedingly complex. Fortunately, in such instances the analyst is often supplied with information concerning the source of the sample, the use for which it is intended, and the claims made for the product. A separation of ingredients usually is not essential to the identification; in fact, the analytical determination (qualitative and quantitative) of one or more typical ingredients may furnish the required information. Moreover, in certain lines of technical analysis, an actual separation of individuals is not necessary, but instead certain analytical procedures are applied directly to the mixture. For example, a sample of oil may be subjected to the following tests:

(*a*) Specific gravity,
(*b*) Melting or solidifying point,
(*c*) Melting-point of acids obtained by saponification,
(*d*) Behavior with solvents,
(*e*) Hehner value (insoluble fatty acids),
(*f*) Reichert-Meissel value (soluble acids),
(*g*) Saponification value,
(*h*) Iodine value, etc.

In dealing with technical samples, the specialized literature of the subject must be consulted. Valuable information will be found in

Allen's Commercial Organic Analysis as well as in the advanced treatises dealing with food, plant, drug, dye, physiological, and toxicological analysis.

Exercises.

Outline in chart form procedures for the separation of the following three mixtures:

1. An aqueous solution containing 1 per cent acetone, 5 per cent glucose, $\frac{1}{2}$ per cent acetic acid, and 1 per cent aniline hydrochloride.

2. A homogeneous liquid containing 50 per cent ethyl alcohol and ether together with aniline, methylaniline, nitrobenzene, and *m*-dinitrobenzene.

3. A solid consisting of salicylic acid, naphthalene, anthranilic acid, β-naphthol, diphenylamine, and sucrose.

PART C

CLASSIFIED TABLES OF COMPOUNDS

The plan for a Solubility Table was presented on page 24 of this text and will be found illustrated in more detail in the chart on the inside rear cover. In connection with a systematic identification of an unknown, the chart may be consulted after the completion of the solubility tests since it may prove of aid in the choice of suitable classification reactions. The tables of individual compounds, however, should not be consulted until the completion of the tests and the systematic elimination of a considerable number of subgroups.

In the tables which follow, approximately two thousand of the more common organic compounds are grouped in accordance with the plan above suggested. The tables are intended only for preliminary aid before proceeding to more advanced reference books and the student is offered no assurance that his unknown is included; his ability to identify unknowns is not limited to a few thousand compounds.

In order to avoid too cumbersome a subdivision, certain subgroups have been united, thus Group I, subgroups 1, 2, 3, and 4 (neutral compounds) are listed in one table, the liquids and solids being presented separately, and subgroups 5, 6, and 7 (acidic substances) are similarly grouped.

Since solubility tests are of qualitative character only, certain compounds near the border line must be listed in more than one place to avoid error. For example, several of the compounds listed on page 189 will be reported normally " insoluble in water " according to the standards set in Chapter VIII. Such compounds, therefore, will be found also in the water-insoluble groups, e.g., Methyl isobutyrate, ethyl propionate, and *n*-propyl acetate are listed in V, 5; methyl propyl ketone and diethyl ketone in V, 3, etc.

Halogen compounds are listed in all groups of the Solubility Table, together with the corresponding unsubstituted compounds without being mentioned specifically as separate subgroups, except under Group VI. No nitrogen or sulfur compounds are included in Groups V and VI, but they are found in the other five groups; elementary analysis automatically relegates an *indifferent* sulfur or nitrogen compound to Group VII.

A few examples will illustrate these points. Ethylene chlorohydrin is placed in Group I, 1, together with ethyl alcohol; the chlorobenzoic and nitrobenzoic acids will be found in Group IV, 1, with other water-insoluble carboxylic acids; and *p*-bromoaniline is included in Group III, 1, with other water-insoluble primary amines. *p*-Nitrobenzoic ethyl ester falls in Group VII, 1, and not in Group V, 5. At the stage of the procedure where the Solubility Table is consulted, it is only known that an indifferent nitrogen group is present; later tests will demonstrate the presence of another indifferent group (ester), but this need not interfere with the classification. *m*-Nitroacetanilide (m.p. 154°) possesses both a nitro and an amide group. It therefore falls under both Group VII, 1 and Group VII, 2 and the student should consult both groups; as a matter of fact, it will be found at both places, but this is not essential.

The tables include practically all of the definite compounds available on the market with the exception of salts, dyes, and certain compounds without melting-points. (See, however, pages 198–199.) In dealing with salts the organic and inorganic constituents are identified separately.

CLASSIFIED TABLES OF COMPOUNDS

(Arranged in Accordance with the Solubility Table)

GROUP I. SUB-GROUPS 1, 2, 3, and 4

Liquids

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
13°	0.894^{0}_{4}	Ethylene oxide
21	0.806^{0}_{4}	Acetaldehyde
32	0.998^{0}_{4}	Methyl formate
35	0.719^{15}_{4}	Ethyl ether
45	0.862^{20}_{4}	Methylal
50	0.806^{20}_{4}	Propionaldehyde
52	0.84	Acrolein
54	0.937^{0}_{4}	Ethyl formate
56	0.800^{15}_{4}	Acetone
57	0.958^{0}_{4}	Methyl acetate
63–4	0.794^{20}_{4}	Isobutyraldehyde
64	0.879^{0}	Dimethylacetal
66	0.792^{20}_{4}	Methyl alcohol
68–70	0.882^{0}	Isopropyl formate
73–4	0.817^{20}_{4}	*n*-Butyraldehyde
77	0.902^{20}_{4}	Ethyl acetate
78	0.785^{25}_{4}	Ethyl alcohol
79	0.937^{0}_{4}	Methyl propionate
80	0.805^{20}	Ethyl methyl ketone
81	0.918^{0}_{4}	*n*-Propyl formate
83	0.948^{18}	Allyl formate
83	0.789^{20}_{4}	Isopropyl alcohol
83	0.780^{26}	*tert*-Butyl alcohol, m. 25°
87–8	0.973^{22}	Diacetyl
89	0.850^{0}	Ethylal
90	1.069^{22}	Methyl carbonate, m. 0°
91	0.917^{0}	Isopropyl acetate
92	0.911^{0}_{4}	Methyl isobutyrate
93–4	0.805^{20}	Isopropyl methyl ketone
97	0.850^{25}_{25}	Allyl alcohol
97	0.804^{20}_{4}	*n*-Propyl alcohol
97–8	1.05–.08	Formalin (40% CH_2O in water)
98	0.914^{0}	Ethyl propionate
98	1.512^{20}_{4}	Chloral
99	0.819^{22}	*sec*-Butyl alcohol
101	0.899^{15}_{4}	*n*-Propyl acetate
101	0.974^{23}	Methyl orthoformate
101–2	0.812^{15}	Methyl propyl ketone
102	0.834^{0}_{4}	Diethyl ketone

GROUP I, SUB-GROUPS 1, 2, 3, and 4—*Continued*

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
102°	0.919^{0}_{4}	Methyl *n*-butyrate
102	0.814^{15}	*tert*-Amyl alcohol
103	0.831^{20}_{4}	Acetal
103	0.938	Allyl acetate
108	0.800^{18}	Isobutyl alcohol
116	0.810^{20}_{4}	*n*-Butyl alcohol
118–9	0.824^{0}	*sec*-Amyl alcohol
119	1.162^{16}	Chloroacetone
120	1.236^{21}	α-Dichloroacetone
124	0.994^{20}_{4}	Paraldehyde, m. 12°
126	0.978^{20}	Ethyl carbonate
130	0.810^{20}_{4}	Isoamyl alcohol
130	1.235^{20}_{20}	Methyl chloroacetate
132	1.223^{0}	Ethylene chlorohydrin
134–6	1.154^{0}	Methyl pyruvate
137	0.973^{25}	Acetylacetone
144	1.118^{0}	Methyl lactate
144 d.		Methyl bromoacetate
145	0.898^{20}_{4}	Ethyl orthoformate
150–2	1.719^{18}	Ethylene bromohydrin
154	1.055^{0}	Ethyl lactate
155	1.060^{16}_{4}	Ethyl pyruvate
155	0.947^{20}_{4}	Cyclohexanone
161	1.159^{20}_{4}	Furfural
162	1.132^{17}	Trimethylene chlorohydrin
164	0.931^{25}	Diacetone alcohol
167		Glycolic acetal
169	1.073^{25}_{25}	Methyl acetoacetate
170	1.135^{20}_{20}	Furfuryl alcohol
172	0.967^{15}	Pinacone m. 35°
174	2.652^{17}	Bromal
176	1.366^{19}	Glycerol α-dichlorohydrin
181	1.160^{15}	Methyl malonate
182		β-Hydroxyethyl acetate
182	1.380^{0}	Glycerol β-dichlorohydrin
186	1.079^{20}_{4}	Ethyl oxalate
191	1.052^{20}	Methyl levulinate
195	1.117^{25}	Methyl succinate, m. 18°
207	1.057^{18}_{4}	γ-Valerolactone
208	1.108^{0}	β-Angelica lactone
210	1.070^{19}	Trimethylene glycol diacetate
100–110/185 mm.		Trimethylene bromohydrin
258	1.161^{15}_{15}	Triacetin
260	1.176^{15}	Diacetin

GROUP I. SUB-GROUPS 1, 2, 3, and 4

Solids

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
12°	124°	Paraldehyde
18	195	Methyl succinate
25	83	*tert*-Butyl alcohol
35	172	Pinacone
44		Bromal alcoholate
48	280	Methyl tartarate
53		Bromal hydrate
55	115	Chloral alcoholate
56		Pinacone hydrate
59	97 d.	Chloral hydrate
79	284 d.	Methyl citrate
83–4		Benzoyl carbinol
86		*o*-Hydroxybenzyl alcohol
86		Diglycolide
116		Benzoquinone
128	255	Lactide

GROUP I. SUB-GROUPS 5*, 6, and 7

Liquids

BOILING-POINT	SPECIFIC-GRAVITY	NAME OF COMPOUND
32°	0.998^{0}_{4}	Methyl formate
54	0.948^{0}_{4}	Ethyl formate
55	1.105^{20}_{4}	Acetyl chloride
57	0.958^{0}_{4}	Methyl acetate
60	1.062^{10}	Chloromethyl ether
63–4		Oxalyl chloride
71	1.236^{15}	Methyl chloroformate
79		Chloromethylethyl ether
80	1.064^{20}_{4}	Propionyl chloride
81	1.52^{9}	Acetyl bromide
92	1.017^{20}_{4}	Isobutyryl chloride
94	1.139^{20}_{20}	Ethyl chloroformate
97		α-Chloroethyl ether
100	1.245^{0}_{4}	Formic acid
100	1.028^{20}_{4}	*n*-Butyryl chloride
105	1.495^{0}	Chloroacetyl chloride
105	1.315^{20}	α, α'-Dichloromethyl ether
115	0.989^{20}_{4}	Isovaleryl chloride
116	1.137^{12}	α, α'-Dichlorodiethyl ether

* Aldehydes (see I, 2) may also show acid reaction due to the presence of oxidation products.

GROUP I. SUB-GROUP 5, 6 and 7—*Continued*

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
118°	$1.054^{\frac{16}{4}}$	Acetic acid, m. 16°
127 (?)	1.913^{9}	Chloroacetyl bromide
127	1.908^{0}	Bromoacetyl chloride
138	1.079^{15}	Acetic anhydride
140	$1.062^{\frac{16}{4}}$	Acrylic acid
140	$0.994^{\frac{20}{20}}$	Propionic acid
144 d.	$1.139^{\frac{15}{15}}$	Propiolic acid
149	2.317^{21}	Bromoacetyl bromide
155	$0.950^{\frac{20}{4}}$	Isobutyric acid
163	$0.960^{\frac{19}{4}}$	*n*-Butyric acid
168	1.017^{15}	Propionic anhydride
165 d.	1.288^{18}	Pyruvic acid
169 d.	1.018^{25}	Isocrotonic acid
176	0.931^{20}	Isovaleric acid
186	1.28^{0}	α-Chloropropionic aicd
189	1.572^{13}	Dichloroacetic acid
190 d.	1.412^{15}	Succinyl chloride, m. 16°
205		α-Bromopropionic acid, m. 24°
250 d.	$1.139^{\frac{20}{4}}$	Levulinic acid

GROUP I. SUB-GROUPS 5, 6 and 7

Solids

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
13°	165° d.	Pyruvic acid
16	118	Acetic acid
16	190 d.	Succinyl chloride
24	205	α-Bromopropionic acid
33	250 d.	Levulinic acid
42		β-Chloropropionic acid
42	180	Phenol
50	208	Bromoacetic acid
54	163	Methyl oxalate
57	195	Trichloroacetic acid
58	288 d.	Orcinol (hydrate)
61–2		β-Bromopropionic acid
63	185	Chloroacetic acid
64	227 d.	α, β-Dibromopropionic acid
66	— d.	Cyanoacetic acid
72	182	α-Crotonic acid
78–9	— d.	Glycolic acid
82		β-Iodopropionic acid
84		Iodoacetic acid

GROUP I. SUB-GROUPS, 5, 6 and 7—*Continued*

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
96°	285° d.	Phenoxyacetic acid
100–10 d.		Peracetic acid
104	245 d.	Catechol
105	272/100 mm.	*n*-Pimelic acid
106	263 d.	Chlorohydroquinone
107	289	Orcinol (anhydrous)
110		Bromohydroquinone
110	280	Resorcinol
111	— d.	Ethylmalonic acid
117 d.		Benzylmalonic acid
118		*dl*-Mandelic acid
124		Trichlorolactic acid
124		Toluhydroquinone
130	— d.	Maleic acid
133		*d*-Mandelic acid *l*-Mandelic acid
133	293 d.	Pyrogallol
133 d.	— d.	Malonic acid
135 d.		Methylmalonic acid
150		Protocatechuic aldehyde
169	285	Hydroquinone
178-9		Acetylenedicarboxylic acid
189	235 d.	Succinic acid
218		Phloroglucinol

GROUP I. SUB-GROUP 8

LIQUIDS

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
−6°	0.699^{-10}	Methylamine
3.5	0.662^{-5}	Trimethylamine
7	0.686^{-6}	Dimethylamine
19	0.689^{15}	Ethylamine
33	0.690^{18}	Isopropylamine
49	0.718^{20}	*n*-Propylamine
55	0.712^{15}	Diethylamine
58	0.769^{15}	Allylamine
63	$0\ \ 18^{20}$	*sec*-Butylamine
68–9	0.736^{15}	Isobutylamine
76–7	0.742^{15}	*n*-Butylamine
95	0.750^{18}	Isoamylamine
103	0.766^{19}	*n*-Amylamine
105	$0.860^{\frac{20}{4}}$	Piperidine
110	0.743^{15}	Di-*n*-propylamine

GROUP I. SUB-GROUP 8—*Continued*

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
111°		Diallylamine
116	$0.976^{\frac{25}{25}}$	Pyridine
129	$0.949^{\frac{15}{4}}$	α-Picoline
133		β-Dimethylaminoethyl alcohol
134	0.86^{20}	Cyclohexylamine
143–50	0.928^{14}	Piperylhydrazine
161		β-Diethylaminoethyl alcohol
184	$0.986^{\frac{15}{15}}$	Benzylamine
189	0.920^{4}	γ-Diethylaminopropyl alcohol
250	$1.011^{\frac{20}{4}}$	*l*-Nicotine

GROUP I. SUB-GROUP 8

SOLIDS

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
41–2°	143°/18 mm.	Cyanamide
63	282	*m*-Phenylenediamine
80 d.		2, 4-Diaminophenol
85		*N*-Methyl-*p*-aminophenol
102	256	*o*-Phenylenediamine
104	145	Piperazine
122		*m*-Aminophenol
140	267	*p*-Phenylenediamine
170		*o*-Aminophenol

GROUP I. SUB-GROUP 9

LIQUIDS

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
17°	0.900^{15}	Ethyl nitrite
65 d.	1.217^{5}	Methyl nitrate
81	0.789^{15}	Acetonitrile
87	1.116^{15}	Ethyl nitrate
97	0.780^{20}	Propionitrile
101	1.144^{15}	Nitromethane
107–8		Isobutyronitrile
120		Acetone cyanohydrin
152 d.	$0.920^{\frac{25}{25}}$	Ethyl methyl ketoxime
182 d.		Lactonitrile
192–5 d.	$1.337^{\frac{14}{4}}$	Formamide, m. 3°
222	$1.024^{\frac{25}{25}}$	Formyl piperidine
226	1.011^{9}	Acetyl piperidine
286	0.995^{15}	Trimethylene cyanide

GROUP I. SUB-GROUP 9

Solids

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
46°	284°	Formanilide
47	114	α-Acetaldoxime
50	184	Ethyl carbamate (Urethane)
52	177	Methyl carbamate
54	265 d.	Succinonitrile
59	195	*n*-Propyl carbamate
60	135	Acetoxime
61	215–20 d.	Trichlorolactonitrile
74–5		Diacetylmonoxime
79	213	Propionamide
81–2	— d.	Phenylhydroxylamine
82	222	Acetamide
113		Antipyrine
114		Chloralformamide
115	216	*n*-Butyramide
125–6	287	Succinimide
128	216	Isobutyramide

GROUP I. SUB-GROUP 10

Liquids

MELTING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
36°	$0.839^{\frac{20}{4}}$	Ethyl mercaptan
93	1.074^{10}	Thioacetic acid
188	1.33^{15}	Methyl sulfate

GROUP I. SUB-GROUP 10

Solids

MELTING-POINT		NAME OF COMPOUND
78°		Allyl thiocarbamide
83–4		Benzenesulfinic acid
109 subl.		Dimethyl sulfone, b. 238°

GROUP II. SUB-GROUP 1

Solids

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
18°	119°/12 mm.	*dl*-Lactic acid
43	255	α-Hydroxybutyric acid
79		Glycolic acid
80		Citraconic acid
97	302 d.	Glutaric acid
100		Citric acid (hydrated)
100		*l*-Malic acid
101		Oxalic acid (hydrated)
130		Maleic acid
132		*dl*-Malic acid
140–3		*i*-Tartaric acid
153		Citric acid (anhydrous)
161		Itaconic acid
169		*d*-Tartaric acid
185	235 d.	Succinic acid
189		Oxalic acid (anhydrous)
190 d.		Aconitic acid
205–6		*dl*-Tartaric acid
212 d.		Mucic acid

GROUP II. SUB-GROUP 2

Liquids

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
188°	1.040^{20}	Propylene glycol
197	$1.113^{\frac{25}{25}}$	Ethylene glycol
210–5 d.	1.338^{0}	Glycerol α-chlorohydrin
216	1.052^{18}	Trimethylene glycol
220–40		Glycerol α-bromohydrin
260	$1.179^{\frac{15}{15}}$	Diacetin
260–70	$1.221^{\frac{15}{15}}$	Monoacetin
290 d.	$1.260^{\frac{20}{4}}$	Glycerol

GROUP II. SUB-GROUP 2

SOLIDS

MELTING-POINT		NAME OF COMPOUND
85–90°		Dextrose (hydrated)
95		Laevulose (*d*-Fructose)
95–7		Glycolic aldehyde
95–105		Rhamnose
110 d.		*d*-Glucosamine
110–20		Raffinose (hydrated)
118–9		Raffinose (anhydrous)
132		*d*-Mannose
144–5		*l*-Xylose
146		Glucose
160		*l*-Arabinose
165		α-Methyl-*d*-glucoside
166		*d*-Mannitol
170		*d*-Galactose
171–2 subl.		Polyoxymethylene
175		Helicin (glucoside)
178 d.		Inulin
185		Saccharose
201		Salicin
203 d.		Lactose
214		Amygdalin
225		*i*-Inosite
234		*d*-Quercite
240° d.		Glycogen
253		Pentaerythrite
— d.		Isomaltose
— d.		Maltose
—		Dextrins

(Some glucosides are listed under V, 1.)

GROUP II. SUB-GROUP 3

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
—	171°	β-Aminoethyl alcohol
	286	Trimethylene cyanide
3°	192–5 d.	Formamide
10	116	Ethylenediamine
44		Piperazine hydrate
54	265 d.	Succinonitrile

GROUP II. SUB-GROUP 3—*Continued*

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
59°		Triacetoneamine (hydrate)
62		Tetramethyl ammonium hydroxide
63	282°	*m*-Phenylenediamine
79	213	Propionamide
80 d.		2, 4-Diaminophenol
82	222	Acetamide
91–4		Acetaldehyde ammonia
101–2	— d.	Methyl urea
102	256	*o*-Phenylenediamine
104	145 (?)	Piperazine
105		Dicyanodiamine (guanyl urea)
110 d.		*d*-Glucosamine
113		Antipyrine
115	216	*n*-Butyramide
122		*m*-Aminophenol
125–6	287–8	Succinimide
128	216	Isobutyramide
132		Carbamide (urea)
140	267	*p*-Phenylenediamine
170		*o*-Aminophenol
170		Malonamide
180		*s*-Acetyl methyl urea
190 d.		Biuret
190 d.		Tetraethyl ammonium hydroxide
195 d.		*dl*-Alanine
205		Dicyanodiamide
216		Hydantoin
218		Acetyl urea
226 d.		*d*-Asparagine *l*-Asparagine
232 d.		Glycocoll
232–40 d.		Choline
234		Caffeine
242 d.		Succinamide
243		Parabain
220+subl.		α-Aminoisobutyric acid
270 d.		*l*-Aspartic acid
280		Hexamethylenetetramine
— d.		Barbituric acid
—		Creatinine
—		Guanidine
—		Alloxan
—		Betain

GROUP II. SUB-GROUP 4

SOLIDS

MELTING-POINT		NAME OF COMPOUND
43–4°		Benzenesulfonic acid (hydrate)
65		Benzenesulfonic acid (anhydrous)
78–9		β–Naphthalenesulfonic acid (trihydrate)
85		Sulfoacetic acid
85–90		α-Naphthalenesulfonic acid
92		*p*-Toluenesulfonic acid
100+		2, 5-Dichlorobenzenesulfonic acid
120		1, 2, 5-Sulfosalicylic acid
122 d.		2-Naphthol-6-sulfonic acid
170 d.		1-Naphthol–4–sulfonic acid
170–4		Thiourea
195 d.		*d*-Camphorsulfonic acid
—		*p*-Phenolsulfonic acid
—		β-Naphthalenesulfonic acid (anhydrous)
259		*p*-Sulfobenzoic acid
—		2-Naphthol-3, 6-Disulfonic acid
—		2–Naphthol-6, 8-Disulfonic acid
—		Many other sulfonic acids, alkyl sulfuric acids, etc., usually met as salts. Cf. List in Eastman Catalogue of Organic Chemicals.

GROUP III. SUB-GROUPS 1, 2, 3

Liquids

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
89°	$0.725^{\frac{25}{25}}$	Triethylamine
110	0.736^{25}	Di-*n*-propylamine
150-5	0.809^{15}	Triallylamine
153	$0.750^{\frac{25}{25}}$	Tri-*n*-propylamine
160		Di-*n*-butylamine
170	0.844^{20}	*d*-Coniine
183	$1.021^{\frac{25}{25}}$	Aniline
180–5		*n*-Octylamine
185	$0.929^{\frac{20}{4}}$	Dimethyl-*o*-toluidine
185		Methyl benzylamine
185		Dimethyl benzylamine
187	$0.766^{\frac{25}{25}}$	Diisoamylamine
192	$0.985^{\frac{25}{25}}$	Methylaniline
193	$0.958^{\frac{20}{4}}$	Dimethylaniline
199	$0.996^{\frac{25}{25}}$	*o*-Toluidine
199		Ethyl benzylamine
201		Ethylmethylaniline
203	$0.989^{\frac{20}{4}}$	*m*-Toluidine
205	$0.963^{\frac{20}{4}}$	Ethylaniline
205	0.86^{20}	*l*-Menthylamine
207	$1.213^{\frac{20}{4}}$	*o*-Chloroaniline
208		*N*-Methyl-*p*-toluidine
210	0.929^{20}	Dimethyl-*p*-toluidine
211	0.778^{20}	Tri-*n*-butylamine
212	0.918^{15}	1, 3-Dimethyl-4-aminobenzene
215	0.980^{15}	1, 4-Dimethyl-2-aminobenzene
218	$0.935^{\frac{20}{4}}$	Diethylaniline
101–2/10 mm.		*N*-Ethyl-*p*-toluidine
124/16 mm.		*N*-Ethyl-*o*-toluidine
220–5	1.098^{15}	*o*-Anisidine (*o*-Methoxyaminobenzene)
222	0.949^{18}	*n*-Propylaniline
229	0.962^{18}	Mesidine
229		*o*-Phenetidine
230	$1.216^{\frac{20}{4}}$	*m*-Chloroaniline
236		*n*-Butylaniline
129/13 mm.		Methyl *N*-methylanthranilate
239	1.095^{20}	Quinoline

GROUP III. SUB-GROUPS 1, 2, 3—*Continued*

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
240°	$1.099^{\frac{20}{4}}$	Isoquinoline, m. 24°
240		3- Bromo-4-aminotoluene
241–45	0.910^{20}	Di-*n*-propylaniline
139–40/15 mm.		Di-*n*-butylaniline
246	1.101^{10}	Quinaldine
245–50	$1.056^{\frac{25}{25}}$	Tetrahydroquinoline
250		*o*-Bromoaniline, m. 31°
251	1.582^{20}	*m*-Bromoaniline, m. 18°
254	$0.928^{\frac{15}{4}}$	Isoamylaniline
254	1.061^{15}	*p*-Phenetidine
258	$1.068^{\frac{20}{4}}$	6-Methyl quinoline
250–60 d.	1.168^{15}	Methyl anthranilate
260–5		Ethyl anthranilate, m. 13°
264	1.061^{15}	2, 4–Dimethyl quinoline
288		Benzyl ethylaniline
293		Methyl α-naphthylamine
294		Ethyl *m*-aminobenzoate
296	$1.048^{\frac{20}{4}}$	Methyl diphenylamine
298	1.067^{15}	Benzylaniline
300	$1.033^{\frac{15}{15}}$	Dibenzylamine
304–5 d.	1.154^{20}	6-Methoxyquinoline
305–6		Benzyl methylaniline

GROUP III. SUB-GROUPS 1, 2, 3

SOLIDS

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
13°	260°	Ethyl anthranilate
15	215–20	Amino-*p*-xylene
18	251	*m*-Bromoaniline
20	250	Tetrahydroquinoline
24	240	Isoquinoline
24.5	135/15 mm.	Methyl anthranilate
25–7		*m*-Iodoaniline
26	240	3- Bromo-4-aminotoluene
28	140/10 mm.	6-Methoxyquinoline
31	250	*o*-Bromoaniline
32	298	Benzylaniline

GROUP III. SUB-GROUPS 1, 2, 3—*Continued*

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
41°	262°	1-Dimethylamino-4-aminobenzene
45	200	*p*-Toluidine
48	—	Tetramethyl *p*-phenylenediamine
49	226	1, 2, 4-Xylidine
50	300	α-Naphthylamine
51	—	Procaine base
52	253–4	Indol
56		*o*-Iodoaniline
57	243	*p*-Anisidine
58	260	4-Phenyl morpholine
60	260–5	2, 6-Dimethyl quinoline
60	280–5	*m*-Nitrodimethylaniline
62	—	*p*-Iodoaniline
63	283	*m*-Phenylenediamine
63	245	2, 4-Dichloroaniline
64		Diphenylethylenediamine
66		*p*-Bromoaniline
68	235	Pseudocumidine
70	300 d.	Dibenzylaniline
70	232	*p*-Chloroaniline
71		*o*-Nitroaniline
72		2-Nitro-*p*-toluidine
73		*p*-Dimethylaminobenzaldehyde
74		Ethyl phenylcinchoninate
75	266	8-Hydroxyquinoline
74–6	165/30 mm.	*p*-Dimethylaminophenol
75–80		Benzamidine
77	262	s-Trichloroaniline
79		2, 4-Dibromoaniline
82	300+	β-Naphtha quinaldine
84		*p*-Nitrosodiethylaniline
85–90		*o*-Methylaminophenol
85		*p*-Methylaminophenol
85	265–8	*m*-Dimethylaminophenol
85		*p*-Nitrosodimethylaniline
86–8		2, 4-Diaminochlorobenzene
88-90		*pp'*-Diaminodiphenylmethane
89		Ethyl-*p*-aminobenzoate
90–1		Tetramethyldiaminodiphenyl-methane

GROUP III. SUB-GROUPS 1, 2, 3—*Continued*

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
91°		Tribenzylamine
91		6-Nitro-*o*-toluidine
95		3-Nitro-*o*-toluidine
98		*l*-Cocaine
99–100		2-Amino-5-azotoluene
102	260	Methyl acetanilide
102	256	*o*-Phenylenediamine
106	293–5	*p*-Aminoacetophenone
107		4-Nitro-2-aminotoluene
107	360+	Acridine
111–2	300	β-Naphthylamine
114	285	*m*-Nitroaniline
114		3-Nitro-*p*-toluidine
114+		*p*-Nitrosomethylaminobenzoate
114–6		*p*-Nitrosomethylaniline
115		Atropine (*dl*-Hyoscyamine)
116		3–Nitro-4-aminotoluene
117		*p*-Dimethylaminoazobenzene
120–1		*s*-Diphenylethylenediamine
122		*m*-Aminophenol
125	360	*p*-Aminoazobenzene
126		Phenylglycine
127	400	Benzidine
127		5-Nitro-2-aminotoluene
129		Methyleneaminoacetonitrile
129		*o*-Tolidine
130 d.		Leucomalachite green
136		Picolinic acid
138		2, 6-Dinitroaniline
140	267	*p*-Phenylenediamine
141		Orthoform
144		Anthranilic acid
144		2-Nitro-1-aminonaphthalene
145		α-Triphenylguanidine
147		*p*-Nitroaniline
147		Papaverine
149		6-Nitroquinoline
155		*l*-Codeine
162		*p*-Aminoacetanilide
163		*p*-Nitrodimethylaniline

GROUP III. SUB-GROUPS 1, 2, 3—*Continued*

MELTING-POINT		NAME OF COMPOUND
163°		Diphenylpiperazine
164		6-Nitroquinaldine
170 d.		*dl*-α-Amino-*n*-caproic acid
170		*o*-Aminophenol
171		Quinidine (dextro)
171–3		Diacetyl morphine
173		5-Amino-*o*-cresol
174		Tetramethyldiaminobenzophenone
174		*m*-Aminobenzoic acid
175		Quinine (lævo)
176		Narcotine (lævo)
178		Brucine (lævo)
180		2, 4-Dinitroaniline
184 d.		*p*-Aminophenol
186		*p*-Aminobenzoic acid
199		2-Hydroxyquinoline
205 (180)		Veratrine
207		Cinchonidine
234 d.		*d*- and *l*-Asparagine
228–30		Nicotinic acid
230		Quinolinic acid
235		Caffeine
250		Morphine (lævo)
250-5		*l*-Aminoanthraquinone
256 subl.		*dl*-Phenylaminoacetic acid
263+ d.		*dl*-Phenylalanine
265		Cinchonine (dextro)
268		Strychnine (lævo)
302		2-Aminoanthraquinone
280–300 d.		*p*-Aminobenzenesulfonic acid (Sulfanilic acid)
310 subl.		Isonicotinic acid
314–8 d.		*l*-Tyrosine
—— d.		5-Aminosalicylic acid
——		Creatin
——		Melamine
subl.		*dl*-α-Aminocaprylic acid
subl.		*dl*-α-Amino-*n*-valeric acid
——		Guanine

GROUP III. SUB-GROUP 4

Liquids

BOILING-POINT	MELTING-POINT	NAME OF COMPOUND
227° d.		*as*-Methylphenylhydrazine
243	17°	Phenylhydrazine

GROUP III. SUB-GROUP 4

Solids

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
44°	220°/40 mm.	*as*-Diphenylhydrazine
61	240-4 d.	*p*-Tolylhydrazine
106		*p*-Bromophenylhydrazine
157 d.		*p*-Nitrophenylhydrazine
210 d.		Anthraquinonylhydrazine
220–5 d.		*p*-Hydrazinobenzoic acid

GROUP IV. SUB-GROUP 1

Liquids

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
176°	0.931^{20}	Isovaleric acid
185	0.941^{20}	*n*-Valeric acid
191	0.978^{15}	*n*-Butyric anhydride
205		α-Bromopropionic acid m. 24°
205	$0.929^{\frac{20}{4}}$	*n*-Caproic acid
207	$0.925^{\frac{20}{4}}$	Isocaproic acid
212–7 d.	1.54^{15}	α-Bromo-*n*-butyric acid
97–105/10 mm.		α-Bromo-*n*-valeric acid
232	$1.048^{\frac{15}{4}}$	Hexahydrobenzoic acid, m. 30°
236	$0.914^{\frac{20}{4}}$	*n*-Caprylic acid, m. 16°
268–70	$0.930^{\frac{35}{15}}$	Capric acid, m. 30°
275 d.	0.910^{25}	Undecenoic acid, m. 24°

GROUP IV. SUB-GROUP 1

Solids

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
14°	285°/100 mm.	Oleic acid
16	236	*n*-Caprylic acid
24	275 d.	Undecenoic acid
—	168/12 mm.	Undecanoic acid
24	205	α-Bromopropionic acid
30	232	Hexahydrobenzoic acid
30	268–70	Capric acid
42	360	Benzoic anhydride
43	225/100 mm.	Lauric acid
48	280	Hydrocinnamic acid
51	234/15 mm.	Elaidic acid
53–4	250/100 mm.	Myristic acid
62	340–50 d.	Palmitic acid
69	360–80	Stearic acid
76	262	Phenylacetic acid
96	285 d.	Phenoxyacetic acid
98	250 d.	Methyl ether salicylic acid
102	259	*o*-Toluic acid
105	272/100 mm.	Pimelic acid
106	360 d.	Nonanedicarboxylic acid (Azelaic)
110	263	*m*-Toluic acid

GROUP IV. SUB-GROUP 1—*Continued*

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
117° d.		Benzylmalonic acid
121	249°	Benzoic acid
126		Phenylglycine
131	284	Phthalic anhydride
132–4	230 d.	Pyromucic acid
133	295/100 mm.	Sebacic acid
133	299 d.	Cinnamic acid
135		Acetylsalicylic acid
136		Dihydroxystearic acid
136		Picolinic acid
136		Phenylpropiolic acid
140		*o*-Chlorobenzoic acid
140		*m*-Nitrobenzoic acid
140		Suberic acid
144		Anthranilic acid
146		*o*-Nitrobenzoic acid
148		*o*-Bromobenzoic acid
148–9		Oxanilic acid
150		Benzilic acid
151		4–Hydroxy-*m*-toluic acid
152		Adipic acid
152		*p*-Nitrophenylacetic acid
155		*m*-Bromobenzoic acid
157		Salicylic acid
158		*m*-Chlorobenzoic acid
158		*o*-Aminocinnamic acid
162		*o*-Iodobenzoic acid
162		α-Naphthoic acid
163		2-Hydroxy-*m*-toluic acid
163–5		*dl*-Benzoyl alanine
170 d.		*dl*-α-Amino-*n*-caproic acid
172-4		Acetylphenylglycine
174		*m*-Aminobenzoic acid
174–5		Propyl Red
175		*p*-Aminocinnamic acid
177		*p*-Toluic acid
179		2, 4-Dinitrobenzoic acid
179		*N*-Methyl anthranilic acid
181–2		Methyl Red
184		Anisic acid
185		β-Naphthoic acid
185		Acetylanthranilic acid

GROUP IV. SUB-GROUP 1—*Continued*

MELTING-POINT		NAME OF COMPOUND
186°		*p*-Aminobenzoic acid
187		*d*-Camphoric acid
187		Hippuric acid
190–200 d.		*o*-Phthalic acid
140 d.–191		3, 6-Dichlorophthalic acid
194		Acetylphenylglycine
196 d.		Protocatechuic acid
196		*m*-Nitrocinnamic acid
200		*m*-Hydroxybenzoic acid
200^{+} subl.		Fumaric acid
200–20 d.		Tannic acid
204		3, 5-Dinitrobenzoic acid
206		*p*-Coumaric acid
207		*o*-Coumaric acid
207		Vanillic acid
210		Phenyl cinchoninic acid
213		*p*-Hydroxybenzoic acid
213–4		*p*-Cyanobenzoic acid
216		2-Hydroxy-3-naphthoic acid
216		Piperic acid
220 d.		2, 4, 6-Trinitrobenzoic acid
220–5 d.		*p*-Hydrazinobenzoic acid
220^{+} d.		Gallic acid
230 d.		*d*- and *l*-Asparagine
228–30		Nicotinic acid
230		Quinolinic acid
237		*o*-Nitrocinnamic acid
237–8 d.		*dl*-α-Aminophenylacetic acid
238		*p*-Nitrobenzoic acid
242 d.		Methylenedisalicylic acid
242		*p*-Chlorobenzoic acid
245 d.		*p*-Hydroxyphenylglycine
249–50		Acetyl-*m*-aminobenzoic acid
252 d.		Acetyl-*p*-aminobenzoic acid
250 d.		Tetrachlorophthalic acid
251		*p*-Bromobenzoic acid
256^{+} subl.		*dl*-Phenylaminoacetic acid
263^{+} d.		*dl*-Phenylalanine
265		*p*-Iodobenzoic acid
274		Naphthalic acid
285		*p*-Nitrocinnamic acid

GROUP IV. SUB-GROUP 1—*Continued*

MELTING-POINT		NAME OF COMPOUND
300°		Isophthalic acid
310 subl.		Isonicotinic acid
314^{+} d.		*l*-Tyrosine
300^{+} subl.		Terephthalic acid
330		α-Naphthophthalein
—— subl.		*dl*-α-Amino-*n*-valeric acid
——		*dl*-α-Aminocaprylic acid
——		5-Aminosalicylic acid

GROUP IV. SUB-GROUP 2

LIQUIDS

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
175°		*o*-Chlorophenol, m. 7°
190	1.051^{15}_{15}	*o*-Cresol, m. 31°
194–5		*o*-Bromophenol
196	1.165^{25}_{25}	Salicylaldehyde
202	1.039^{15}_{15}	*p*-Cresol, m. 36°
202	1.039^{15}_{15}	*m*-Cresol
205	1.153^{0}	Guaiacol, m. 28°
211	1.036^{0}	1, 3, 4-Xylenol, m. 26°
214		*m*-Chlorophenol, m. 28°
224	1.189^{15}_{15}	Methyl salicylate
230	1.184^{20}	Ethyl salicylate
236		*m*-Bromophenol, m. 32°
237	0.978^{20}_{20}	Carvacrol
238 d.	1.098^{15}	*n*-Propyl salicylate
243	1.070^{4}	Resorcinolmonomethyl ether
250	1.069^{15}_{15}	Eugenol
250	1.065^{15}	Isoamyl salicylate
153/10 mm.	———	Resorcinol monacetate
267	1.090^{15}_{15}	Isoeugenol

GROUP IV. SUB-GROUP 2

Solids

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
26°	211°	1, 3, 4-Xylenol
28	205	Guaiacol
28	214	*m*-Chlorophenol
31	190	*o*-Cresol
32	236	*m*-Bromophenol
36	202	*p*-Cresol
37	217	*p*-Chlorophenol
42	180	Phenol
42	172/12 mm.	Phenyl salicylate
45	214	*o*-Nitrophenol
49	211	1, 3, 2-Xylenol
50	232	Thymol
52–3	236	6-Chloro-*m*-cresol
53	243	Hydroquinonemonomethyl ether
60		1, 2-Dihydroxynaphthalene
63	236	*p*-Bromophenol
65	225	1, 2, 4-Xylenol
67	244	*s*-Trichlorophenol
68	219	Hydroxymesitylene
70		Methyl *m*-hydroxybenzoate
71	234	Pseudocumenol (1, 2, 4-Trimethyl-5-hydroxybenzene)
72	282	*m*-Hydroxyethylbenzoate
74	211	1, 4, 2-Xylenol
75	266	8-Hydroxyquinoline
74–6	165/30 mm.	*p*-Dimethylaminophenol
80	285	Vanillin
80 d.		*o*-Methylaminophenol
81		2-Hydroxy-1-naphthylaldehyde
85		*p*-Methylaminophenol
85	265–8	*m*-Dimethylaminophenol
93		*m*-Nitrophenol
94	278–80	α-Naphthol
96		*s*-Tribromophenol
104		*m*-Hydroxybenzaldehyde
109		α-Nitroso-β-naphthol
110		Bromohydroquinone
114		*p*-Nitrophenol
114		2, 4-Dinitrophenol
115		*p*-Hydroxybenzaldehyde
116	298	*p*-Hydroxyethylbenzoate

GROUP IV. SUB-GROUP 2—*Continued*

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
122°		Picric acid
122	285°	β-Naphthol
122		*m*-Aminophenol
125 d.		*p*-Nitrosophenol
128–30		Benzeneazo-*o*-cresol
131	270 d.	*p*-Hydroxymethylbenzoate
140		Salicylamide
140		1, 8-Dihydroxynaphthalene
147–8 d.		β-Nitroso-α-naphthol
150		Ethyl gallate
150		Protocatechuic aldehyde
151		4-Hydroxy-*m*-toluic acid
152		*p*-Hydroxyazoxybenzene
162		*p*-Hydroxybenzamide
165		Arbutin (Glucoside)
166		N-Acetyl-*p*-aminophenol
168		2, 4-Dinitro-6-aminophenol
168–9		N-Acetyl-*p*-methylaminophenol
169–70		Dichlorohydroquinone
170		*o*-Aminophenol
170		*m*-Hydroxybenzamide
170–90		Aurin
171		Quinhydrone
171		*o*-Azophenol
173		5-Amino-2-hydroxytoluene
176		1, 4-Dihydroxynaphthalene
181		1, 4-Naphtholaldehyde
184 d.		*p*-Aminophenol
185		*p*-Benzalaminophenol
190		1, 4-Nitrosonaphthol
192 d.		Thymolphthalein
199		2-Hydroxyquinoline
201		N-Acetyl-*o*-aminophenol
204		*p*-Azophenol
210		Tetrabromo-*o*-cresol
210–11		5-Benzalamino-*o*-cresol
213		*o*-Cresolphthalein
218		Phloroglucinol
250–3		Phenolphthalein
289		Alizarin
290+		Fluorescein

GROUP IV. SUB-GROUP 3

Solids

MELTING-POINT		NAME OF COMPOIND
172°		Phenyl ethyl barbituric acid
188		Diethyl barbituric acid
200		Isatin
230 d.		Nitroguanidine
233		Phthalimide
—— d.		Nitro urea
270		Theophyllin
300 subl.		Theobromine
——		Cyanuric acid
——		Uric acid

GROUP IV. SUB-GROUP 4

Liquids

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
101°	1.144^{15}	Nitromethane
114	1.056^{15}	Nitroethane
130	1.022^{4}	*n*-Nitropropane
226 d.	1.160^{20}	Phenylnitromethane

GROUP IV. SUB-GROUP 4

Solids

MELTING-POINT		NAME OF COMPOUND
33–5°		α-Benzaldoxime
59		Acetophenone oxime
82		Trinitrotoluene
109		α-Nitroso-β-naphthol
120		*d*-Camphor oxime
125		*p*-Nitrosophenol
140		Benzophenone oxime
144		*p*-Nitrosodiphenylamine
235		Diacetyldioxime(Dimethylglyoxime)
237 d.		α-Benzildioxime

GROUP IV. SUB-GROUP 5

SOLIDS

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
—	170°	Thiophenol
—	195	*m*-Thiocresol
15°	194	*o*-Thiocresol
24	— d.	Thiobenzoic acid
43	194	*p*-Thiocresol
81	286	β-Thionaphthol
83–4		Benzenesulfinic acid
85		*p*-Toluenesulfinic acid
88		Benzenesulfonyl benzylamine
95		Benzenesulfonyl-*m*-toluidine
101		*p*-Toluenesulfonylaniline
104		Benzenesulfonyl-*o*-nitraniline
112		Sulfanilide
112		Benzenesulfonylaniline
115		Thiobenzamide
117		*p*-Toluenesulfonyl-*p*-toluidine
120		Benzenesulfonyl-*p*-toluidine
121		Benzenesulfonyl-*p*-chloroaniline
124		Benzenesulfonyl-*o*-toluidine
132		Benzenesulfonyl-*m*-nitraniline
136		*p*-Toluene sulfonamide
139		Benzenesulfonyl-*p*-nitraniline
150		α-Napthalenesulfonamide
154		*o*-Toluene sulfonamide
156		Benzenesulfonamide
157		Phenylthiohydantoic acid
164		Thiosalicylic acid
217		β-Napthalenesulfonamide
220 d.		*o*-Benzoic sulfimide (Saccharin)
240 d.		Thiobarbituric acid
—		*l*-Cystine
—		Many sulfonic acids, such as sulfanilic, aminonaphthalene sulfonic, etc.
—		Sulfonephthaleins, such as phenolsulfonephthalein, thymolsulfonephthalein, dibromothymolsulfonephthalein, *o*-cresolsulfonephthalien etc.

GROUP IV. SUB-GROUP 6

Liquids

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
169°	1.081^{15}	Methyl acetoacetate
181	$1.026^{\frac{20}{4}}$	Ethyl acetoacetate

GROUP IV. SUB-GROUP 6

Solids

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
60°	262–4°	Benzoylacetone
80		Dibenzoylmethane
108–9	270	Dehydracetic acid

GROUP V. SUB-GROUPS 1, 2, 3

Liquids

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
92	0.804^{15}	Isovaleraldehyde
100–1	0.814^{15}	*tert*-Amyl alcohol
101	0.812^{15}	Methyl propyl ketone
102	0.833^{0}_{4}	Diethyl ketone
103	0.818^{11}	*n*-Valeraldehyde
10[illegible]	0.826^{0}	Pinacoline
116	1.203^{0}_{4}	α-Epichlorohydrin
116–8	—	Methyl *n*-propyl carbinol
118	0.823^{0}	*sec*-Amyl alcohol
119	0.803^{19}	Isobutyl methyl ketone
124	0.994^{20}_{4}	Paraldehyde, m. 12°
127–8	0.833^{20}	*n*-Hexyl aldehyde
129–31	0.810^{20}	Isoamyl alcohol
130	0.858^{20}_{4}	Mesityl oxide
130–1	0.942^{21}_{4}	Cyclopentanone
136	0.833^{0}	*sec*-Hexyl alcohol
136–9		*n*-Butyl methyl carbinol
137	0.817^{20}	*n*-Amyl alcohol
139	0.940^{21}	Cyclopentanol
142		Triethyl carbinol
151	0.837^{0}	Methyl *n*-amyl ketone
155	0.947^{20}_{4}	Cyclohexanone
155–6	0.849^{20}_{4}	*n*-Heptylaldehyde
157–8	0.820^{20}	*n*-Hexyl alcohol
160	0.944	Cyclohexanol, m. 16°
165–70		Methyl cyclohexanols
175–6	0.830^{16}	*n*-Heptyl alcohol
176	1.396^{16}	Glycerol α-dichlorohydrin
179	0.819^{20}_{4}	*sec*-Octyl alcohol
179	1.050^{15}_{4}	Benzaldehyde
179–81	0.969^{0}	Cycloheptanone
180		*n*-Hexyl methyl carbinol
182	1.380^{0}	Glycerol β-dichlorohydrin
94–5/15 mm.		Di-*n*-butyl carbinol
190–5	0.870^{20}	*l*-Linalool
192	0.837^{0}	*n*-Octyl alcohol (primary)
198	0.885^{20}_{4}	Phorone, m. 28°
199	1.024^{22}	*m*-Toluylaldehyde
98–100/35 mm.		Para *n*-butyraldehyde

GROUP V. SUB-GROUPS 1, 2, 3—*Continued*

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
200°		*o*-Toluylaldehyde
200	1.023^{25}	Acetophenone, m. 20°
203	1.013	Methyl phenyl carbinol
205	$1.050^{\frac{15}{15}}$	Benzyl alcohol
205–8	0.856^{20}	Citronellal
207	0.896^{20}	*l*-Menthone
114–8/15 mm.		Tri-*n*-butyl carbinol
213–4	1.29^{8}	*o*-Chlorobenzaldehyde
213–4		*m*-Chlorobenzaldehyde, m. 17°
218	0.935^{20}	Terpineol, m. 35°
219	1.024^{15}	β-Phenylethyl alcohol
219	2.168^{0}	Glycerol-β-dibromohydrin
219 d.	2.11^{18}	Glycerol-α-dibromohydrin
220 d.	$1.050^{\frac{24}{4}}$	Cinnamaldehyde
222	1.013	Methyl-*p*-tolyl ketone
224–8 d.	0.897^{15}	Citral
113–4/15 mm.	0.861^{20}	Rhodinol
229	0.883^{15}	Geraniol
231	$0.839^{\frac{7}{4}}$	*n*-Decyl alcohol
235	1.008^{18}	Phenylpropyl alcohol
241–2		*o*-Methoxybenzaldehyde
248	1.123^{18}	Anisaldehyde, m. 0°
143/15 mm.	$0.831^{\frac{24}{4}}$	Lauryl alcohol, m. 24°
143–5/15 mm.	0.904	Pseudoionone
250	$1.030^{\frac{36}{4}}$	Cinnamyl alcohol, m. 33°
262		Benzalacetone, m. 41°
174–81/10 mm.		Dibenzyl ketone

GROUP V. SUB-GROUPS 1, 2, 3

SOLIDS

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
12°	124°	Paraldehyde
16	160	Cyclohexanol
16–8	105–7/14 mm.	Propiophenone
20	200	Acetophenone
24	143/15 mm.	Lauryl alcohol
28	198	Phorone
33	250	Cinnamyl alcohol

GROUP V. SUB-GROUP 1, 2, 3—*Continued*

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
35°	218°	Terpineol
35	243	*o*-Methoxybenzaldehyde
37	263	Piperonal
39		Myristyl alcohol
40–1		α, γ-Dichloroacetone
41	262	Benzalacetone
42	212	*l*-Menthol
45	259	Anisic alcohol
47	213	*p*-Chlorobenzaldehyde
48	305	Benzophenone
50	344	Cetyl alcohol
50		ω-Bromoacetophenone
52–4		Phenyl *p*-tolyl ketone
55–6		*o*-Phthaldehyde
57		Benzalacetophenone
59	244	ω-Chloroacetophenone
60		β-Naphthaldehyde
68		Toluquinone
70–1		2, 4-Dichlorobenzaldehyde
76	274	α-Bromo-*d*-camphor
77–8		Trichloro-*tert*-butyl alcohol
78		Butyl chloral hydrate
80	285 d.	Vanillin
91–2		Di-*p*-tolyl ketone
95	347	Benzil
102	285	Terpin
112		Dibenzylidineacetone
112–5 subl.		Metaldehyde
115		*p*-Hydroxybenzaldehyde
115–20 d.		β-Naphthoquinone
116		Benzoquinone
116	245–8	Terephthaldehyde
117		Terpin hydrate
125		α-Naphthoquinone
137	343	Benzoin
148		*l*-Cholesterol
162	360	Triphenylcarbinol
167		Tribromo-*tert*-butyl alcohol
171–2 subl.		Polyoxymethylene
173		Xanthone
176	205	*d*-Camphor
177		2-Methyl anthraquinone
178		*dl*-Camphor

GROUP V SUB-GROUPS 1, 2, 3—*Continued*

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
180°		Populin (Glucoside)
185		Coniferin (Glucoside)
198		Camphorquinone
201		Salicin (Glucoside)
202	360°	Phenanthraquinone
204	212	*d*-Borneol
261		Acenaphthoquinone
273 (280)	380	Anthraquinone
290 subl.		Chloranil (Tetrachlorobenzoquinone)

GROUP V. SUB-GROUP 4

LIQUIDS

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
35°	$0.719^{\frac{15}{4}}$	Ethyl ether
45	$0.872^{\frac{15}{4}}$	Methylal
64		Dimethylacetal
69	0.724^{20}	Diisopropyl ether
73–4	$0.817^{\frac{20}{4}}$	*n*-Butyraldehyde
89		Ethylal
97–101		*n*-Amyl methyl ether
101		Methyl orthoformate
102	$0.831^{\frac{20}{4}}$	Acetal
116	1.138^{12}	α, α'-Dichloroethyl ether (sym.)
116	$1.203^{\frac{0}{4}}$	Epichlorohydrin
124	$0.994^{\frac{20}{4}}$	Paraldehyde
140	0.769^{20}	*n*-Butyl ether
140	1.174^{23}	α, β-Dichloro diethyl ether
145	$0.896^{\frac{20}{4}}$	Ethyl orthoformate
154	$0.988^{\frac{20}{4}}$	Anisole
157	1.026^{15}	Monochloroacetal
167	0.981^{4}	Benzyl methyl ether
170		Monobromoacetal
171	0.996^{0}	*o*-Cresyl methyl ether
172	$0.774^{\frac{25}{25}}$	Isoamyl ether
172	0.979^{4}	Phenetole
174–6	0.922	Cineol
175–8		β, β'-Dichloroethyl ether
176	0.987^{0}	*p*-Cresyl methyl ether

GROUP V. SUB-GROUP 4—*Continued*

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
177°	0.985^{4}	*m*-Cresyl methyl ether
185		Benzyl ethyl ether
187–90		*n*-Amyl ether
195		*o*-Chloroanisole
200		*p*-Chloroanisole
206	1.086^{15}	Veratrole (1, 2-Dimethyoxybenzene) m. 15°
208		*o*-Chlorophenetole
210	0.950	*n*-Butyl phenyl ether
212		*p*-Chlorophenetole, m. 20°
212		Benzyl isobutyl ether
213–6		Benzyl *n*-butyl ether
214	$1.080\frac{0}{4}$	Resorcinyl dimethyl ether
216	0.954^{0}	Thymyl methyl ether
218		*o*-Bromoanisole
223	0.944^{0}	*n*-Butyl *o*-cresyl ether
223	1.494^{9}	*p*-Bromoanisole
224		*o*-Bromophenetole
229		*p*-Bromophenetole
232	1.096^{18}	Safrole
232	0.989^{28}	Anethole, m. 21°
244	1.055^{15}	Eugenol methyl ether
246	1.125^{14}	Isosafrole
252	1.073^{20}	Diphenyl ether, m. 28°
265	1.096^{14}	α-Naphthyl methyl ether
278	1.074	α-Naphthyl ethyl ether
282		β-Naphthyl ethyl ether, m. 37°
178–9/11 mm.		β-Naphthyl isoamyl ether, m. 26°
298	1.036^{16}	Dibenzyl ether

GROUP V. SUB-GROUP 4

Solids

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
15°	207°	Veratrole
20	212	*p*-Chlorophenetole
21	232	Anethole
26	325	β-Naphthyl isoamyl ether
28	252	Diphenyl ether
32	300	Apiole
37	282	β-Naphthyl ethyl ether
43	246	*s*-Trichlorophenetole
55	212	Hydroquinone dimethyl ether
60	240	*s*-Trichloroanisole
72	274	β-Naphthyl methyl ether
72		*s*-Tribromophenetole
87		*s*-Tribromoanisole

GROUP V. SUB-GROUP 5

Liquids

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
72–5°	$1.218^{\frac{25}{25}}$	Methyl chlorocarbonate
77	$0.924^{\frac{0}{4}}$	Ethyl acetate
90	1.069^{22}	Methyl carbonate, m. 0°
92	$0.911^{\frac{0}{4}}$	Methyl isobutyrate
93	1.144^{15}	Ethyl chlorocarbonate
98		Isobutyl formate
98	0.914^{0}	Ethyl propionate
101	$0.899^{\frac{15}{4}}$	*n*-Propyl acetate
102	$0.919^{\frac{0}{4}}$	Methyl *n*-butyrate
103	0.938	Allyl acetate
107	0.911^{0}	*n*-Butyl formate
110	$0.890^{\frac{0}{4}}$	Ethyl isobutyrate
111	0.892	*sec*-Butyl acetate
113		*n*-Propyl chlorocarbonate
116	$0.892^{\frac{0}{4}}$	Isobutyl acetate
116	$0.900^{\frac{0}{4}}$	Methyl isovalerate
120	$0.899^{\frac{0}{4}}$	Ethyl *n*-butyrate
122	$0.902^{\frac{0}{4}}$	*n*-Propyl propionate
123	$0.894^{\frac{0}{4}}$	Isoamyl formate
125	0.882^{20}	*n*-Butyl acetate
126	$0.976^{\frac{20}{4}}$	Ethyl carbonate

GROUP V. SUB-GROUP 5—*Continued*

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
127–30°	0.910^{0}	Methyl *n*-valerate
128	0.879^{0}	Isopropyl *n*-butyrate
130	1.235^{20}_{20}	Methyl chloroacetate
134	0.885^{0}_{4}	Ethyl isovalerate
137	0.892^{0}_{4}	Isobutyl propionate
140–5		*n*-Butyl chlorocarbonate
142	0.876^{15}_{4}	Isoamyl acetate
143	0.893^{0}	*n*-Propyl *n*-butyrate
144 d.		Methyl bromoacetate
145	0.876^{20}	Ethyl *n*-valerate
145	1.158^{20}_{4}	Ethyl chloroacetate
145	1.178	β-Chloroethyl acetate
145	0.847^{19}	Ethyl orthoformate
146	1.087^{20}_{4}	Ethyl α-chloropropionate
147	0.875^{0}_{4}	Isobutyl isobutyrate
150–2	1.031^{20}	Ethyl lactate
157	0.888^{0}_{4}	Isobutyl *n*-butyrate
158	1.282^{20}_{4}	Ethyl dichloroacetate
159	1.507^{25}_{25}	Ethyl bromoacetate
160	0.888^{0}_{4}	Isoamyl propionate
162	1.393^{20}	Ethyl α-bromopropionate
164–6		*n*-Propyl carbonate
165	0.888	*n*-Butyl *n*-butyrate
167		α-Angelica lactone, m. 18–19°
167	1.383^{20}	Ethyl trichloroacetate, m. 141°
167	0.873^{20}	Ethyl *n*-caproate
170	1.073^{25}_{25}	Methyl acetoacetate
171–6		Cyclohexylacetate
174–6		Methyl *n*-heptylate
177	1.020^{90}	Methyl methylacetoacetate
178	1.107^{15}	Methyl methylmalonate
178	0.882^{0}_{4}	Isoamyl butyrate
180	1.081^{15}	*n*-Butyl chloroacetate
181	1.024^{20}_{4}	Ethyl acetoacetate
181	1.160^{15}	Methyl malonate
83–5/20 mm.		*o*-Cresyl acetate
186	1.076^{25}_{25}	Ethyl oxalate
186	1.128^{0}	Ethyleneglycoldiacetate
187	1.009^{6}	Ethyl methylacetoacetate
190	0.995^{14}	Methyl ethylacetoacetate
67–70/8 mm.		Ethyl *n*-heptylate
191		Methyl levulinate
193	0.887^{18}	Methyl caprylate

GROUP V. SUB-GROUP 5—*Continued*

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
194°	0.870^{0}	Isoamyl isovalerate
196	1.021^{15}	Ethyl methylmalonate
196	1.093^{0}_{4}	Phenyl acetate
198	1.054^{25}_{25}	Ethyl malonate
198	1.04^{15}_{4}	Methyl benzoate
198	0.998^{12}	Ethyl ethylacetoacetate
90–1°/14 mm.		Isopropyl oxalate
202	1.016^{20}	Ethyl levulinate
205	0.924^{20}	Butyl carbonate
100–5/15 mm.	0.895^{20}	Linalyl acetate
108–10/10 mm.		Ethyl *n*-butylmalonate
206 (215–6)	$1.057^{16.5}$	Benzyl acetate
207	1.005^{18}_{15}	Ethyl ethylmalonate
207	0.887^{0}	Ethyl caprylate
210	0.885	*sec*-Octyl acetate
211		Phenyl propionate, m. 20°
213	1.038^{0}	*n*-Propyl oxalate
213	1.054^{25}_{25}	Ethyl benzoate
217	1.044^{15}	Ethyl succinate
218	1.017^{15}_{15}	Isopropyl benzoate
220	1.044^{16}	Methyl phenylacetate
221		Bornyl acetate, m. 29°
223		Methyl caprate
110–12/10 mm.		Ethyl caprate
226	1.046^{15}_{15}	Ethyl phenylacetate
227	0.985^{20}_{0}	*l*-Menthyl acetate
129–30/8 mm.		Ethyl di-*n*-butylmalonate
228		Methyl *o*-methoxybenzoate
128–32/18 mm.		*n*-Butyl phenylacetate
128–30/20 mm.		Isobutyl phenylacetate
133–4/20 mm.		Ethyl glutarate
230	1.032^{16}	*n*-Propyl benzoate
230	1.058^{15}_{15}	Allyl benzoate
230		Ethyl diethylmalonate
127–9/8 mm.		Methyl laurate
233–5	1.426^{15}	Ethyl bromomalonate
131–2/15 mm.		Ethyl adipate
235		β, β'-Dichloroethyl carbonate
235–7	1.137^{15}_{15}	Ethyl salicylate
238	1.033^{16}	Benzyl *n*-butyrate
241	1.003^{15}_{15}	Isobutyl benzoate
243	1.010^{0}	*n*-Butyl oxalate

GROUP V. SUB-GROUP 5—*Continued*

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
245°	1.009^{0}	Thymyl acetate
245	1.150^{17}	Methyl phenoxyacetate
154–5/15 mm.		*n*-Butyl salicylate
246	1.016^{4}	*n*-Propyl succinate
249	1.000^{20}	*n*-Butyl benzoate
251	1.104^{17}	Ethyl phenoxyacetate
260	$1.159^{\frac{25}{25}}$	Triacetin
262	1.004^{0}	Isoamyl benzoate
262	0.968^{11}	Isoamyl oxalate
263	$1.042^{\frac{36}{0}}$	Methyl cinnamate, m. 36°
265	0.974^{15}	Isobutyl succinate
265–70		γ, γ'-Dichloropropyl carbonate
269	0.867^{19}	Ethyl laurate
269–70	1.119^{4}	Ethyl anisate, m. 7°
185–6/50 mm.		*n*-Butyl *o*-methoxybenzoate
270	$1.045^{\frac{25}{25}}$	Isoamyl salicylate
270		Methyl aconitate
271	1.050^{20}	Ethyl cinnamate, m. 12°
196–8/15 mm.		*n*-Butyl tartarate
275	1.130^{20}	Isopropyl tartarate
275	1.074^{14}	Ethyl aconitate
278 d.		Resorcinol diacetate
280	1.206^{20}	Ethyl tartarate
282	$1.189^{\frac{25}{25}}$	Methyl phthalate
283	1.034^{16}	Ethyl benzylacetoacetate
285	1.032^{20}	Glycerol tributyrate
288		Methyl sebacate, m. 38°
208/26 mm.		Benzyl salicylate
294	$1.137^{\frac{20}{4}}$	Triethyl citrate
295	$1.118^{\frac{20}{4}}$	Ethyl phthalate
152–5/10 mm.		Isopropyl phthalate
297	0.961^{13}	Isoamyl succinate
300	1.077^{15}	Ethyl benzylmalonate
307		*o*-Cresyl benzoate
307	0.965^{16}	Ethyl sebacate
323	1.114^{18}	Benzyl benzoate
204/5 2mm.		Tributyrin
243–6/18 mm.	$1.093^{\frac{20}{4}}$	Ethyl dibenzylmalonate
— d.		Trioleine

GROUP V. SUB-GROUP 5

SOLIDS

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
10–15°		Dioleine
12	271°	Ethyl cinnamate
13	250/40 mm.	Ethyl dibenzylmalonate
14		Cinnamyl cinnamate
15–20		Monoleine
16–17		Methyl myristate
20	211	Phenyl propionate
27–8		Methyl palmitate
29	221	Bornyl acetate
30		Benzyl cinnamate
33		Thymyl benzoate
36	263	Methyl cinnamate
37	254	Ethyl mandelate
37–8		Methyl stearate
42		Benzyl succinate
42		Benzyl phthalate
45	255	Methyl anisate
49–50	245/11 mm.	Triphenylphosphate
52		Methyl mandelate
54		Trimyristin
54		*l*-Menthyl benzoate
55		*m*-Cresyl benzoate
60		Guaiacol benzoate
61		Monostearine
61		Dipalmitine
63		Monopalmitine
65	233-7	Tripalmitine
66	290	Ethyl trichlorolactate
67		Coumarin
68-9		Phenyl benzoate
70		Phenyl phthalate
71		Tristearine
71	205–7/15 mm.	*p*-Cresyl benzoate
72		Phenyl cinnamate
73	290	Glycol dibenzoate
73		Phthalide
76	301	Distearine
78	284	Diphenyl carbonate
78–9		Methyl citrate
80		Benzyl oxalate
83		Guaiacol carbonate
86		Diglycolide

GROUP V. SUB-GROUP 5—*Continued*

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
93°		β-Naphthyl salicylate
107		β-Naphthyl benzoate
123		Hydroquinone diacetate
127	255°	Lactide
161		Pyrogallol triacetate
170		Santonin
223		Polyglycolide

GROUP V. SUB-GROUP 6

LIQUIDS

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
100°	$1.028^{\frac{20}{4}}$	*n*-Butyryl chloride
115	$0.989^{\frac{20}{4}}$	Isovaleryl chloride
191	0.978^{15}	*n*-Butyric anhydride
197	$1.212^{\frac{20}{4}}$	Benzoyl chloride
102/17 mm.	$1.168^{\frac{24}{4}}$	Phenyl acetyl chloride
213	1.242^{25}	Citraconic anhydride
218	1.570^{15}	Benzoyl bromide
145/14 mm.		Anisyl chloride, m. 26°
254		*o*-Methoxybenzoyl chloride
276	$1.409^{\frac{20}{4}}$	Phthalyl chloride, m. 14°

GROUP V. SUB-GROUP 6

SOLIDS

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
26°	145°/14 mm.	Anisyl chloride
35–6	154/25 mm.	Cinnamoyl chloride
42	360	Benzoic anhydride
53	202	Maleic anhydride
85		Diphenylcarbamide chloride
103		Benzoyl peroxide
120	260	Succinic anhydride
130		Cinnamic anhydride
131	284	Phthalic anhydride
220	270	*d*-Camphoric anhydride
274		Naphthoic anhydride

GROUP V. SUB-GROUP 7

Liquids

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
21°		3-Methylbutene-1
22–37	$0.66^{\frac{15}{15}}$	Amylene (techn.)
35–8	0.678^{0}	Isoamylene
42	$0.805^{\frac{19}{4}}$	Cyclopentadiene
58–9	$0.690^{\frac{20}{4}}$	Diallyl
102–4		2-Methyl cyclohexene
102–4		3-Methyl cyclohexene
107–9		4-Methyl cyclohexene
146	0.925	Styrene
155–60	0.858^{20}	Pinene
160–70	0.860^{25}	Terebene
167	$0.814^{\frac{20}{4}}$	Menthene
176	0.846^{18}	Limonene
176	0.851^{16}	Sylvestrene
176-7	$0.914^{\frac{15}{15}}$	Allyl benzene
180	1.040^{15}	Indene
181	0.854^{16}	Dipentene
212		Dihydronaphthalene
232		Safrole
244	$1.035^{\frac{25}{25}}$	Eugenyl methyl ether
246–8		Isosafrole

GROUP V. SUB-GROUP 7

Solids

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
15°	212°	Dihydronaphthalene
51	160	*l*-Camphene
125	306	Stilbene

GROUP VI. SUB-GROUPS 1 and 2

Liquids

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
30–1°	$0.613^{\frac{1}{4}}$	Isopentane
30–50	$0.62\text{–}.63^{25}$	Petroleum ether (mixture)
36	0.645^{0}	Pentane
50–70	$0.63\text{–}.66^{25}$	Benzine (ligroin mixture)
68	$0.660^{\frac{20}{4}}$	*n*-Hexane
70–100+	$0.70\text{–}.75^{25}$	Gasoline (mixture) Ligroin (mixture)
80	$0.874^{\frac{20}{4}}$	Benzene, m. 5°
80	$0.790^{\frac{20}{4}}$	Cyclohexane, m. 4°
100	$0.769^{\frac{20}{4}}$	Methyl cyclohexane
111	$0.881^{\frac{4}{4}}$	Toluene
125	$0.719^{\frac{0}{4}}$	*n*-Octane
135	$0.876^{\frac{10}{4}}$	Ethyl benzene
137	$0.866^{\frac{14}{4}}$	*p*-Xylene, m. 15°
139	$0.871^{\frac{12}{4}}$	*m*-Xylene
142	$0.890^{\frac{4}{4}}$	*o*-Xylene
150–300	$0.78\text{–}.82^{25}$	Kerosene (mixture)
153	$0.875^{\frac{4}{4}}$	Cumene (Isopropyl benzene)
156–8	$0.735^{\frac{10}{4}}$	Diisoamyl (decane)
158	$0.870^{\frac{10}{4}}$	Propyl benzene
164	$0.869^{\frac{10}{4}}$	Mesitylene
167–9	0.796^{15}	*p*-Menthane
168	0.889^{4}	Pseudocumene
175	0.852^{25}	*p*-Cymene
180	1.040^{15}	Indene
182	$0.860^{\frac{20}{4}}$	Diethyl benzene (*o*, *m*, and *p*)
240	1.001^{19}	α-Methyl naphthalene
242		β-Methyl naphthalene, m. 32°
261	$1.001^{\frac{26}{4}}$	Diphenylmethane, m. 26°

GROUP VI. SUB-GROUPS 1 and 2

Solids

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
15°	137°	*p*-Xylene
26–7	261	Diphenylmethane
32	242	β-Methyl naphthalene
52	284	Dibenzyl
70	254	Diphenyl
80	218	Naphthalene
92	359	Triphenylmethane
95 (103)	277	Acenaphthene
100	340	Phenanthrene
115	295	Fluorene
125	306	Stilbene
213	360	Anthracene

GROUP VI. SUB-GROUPS 3 and 4

Liquids

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
12–3°	0.921^{0}	Ethyl chloride
36	0.859^{20}	Isopropyl chloride
38	1.450^{15}	Ethyl bromide
42	1.378^{0}_{4}	Methylene chloride
43	2.285^{15}	Methyl iodide
46	0.892^{20}	*n*-Propyl chloride
46	0.955^{0}	Allyl chloride
51	0.847^{15}	*tert*-Butyl chloride
55		Acetylene dichloride
60	1.180^{22}	Ethylidene chloride
60	1.310^{20}	Isopropyl bromide
61	1.504^{12}	Chloroform
68	0.880^{15}	Isobutyl chloride
70		2, 2-Dichloropropane
70	1.436^{15}	Allyl bromide
71	1.352^{20}	*n*-Propyl bromide
72	1.202^{15}	*tert*-Butyl bromide
72	1.943^{15}_{15}	Ethyl iodide

GROUP VI. SUB-GROUPS 3 and 4—*Continued*

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
74°	$1.325^{\frac{26}{4}}$	1, 1, 1-Trichloroethane
77	0.887^{20}	*n*-Butyl chloride
78	$1.591^{\frac{25}{25}}$	Carbon tetrachloride
83	1.667^{16}	1-Chloro-1-bromoethane
83	1.256^{20}	Ethylene chloride
86	0.870^{19}	*tert*-Amyl chloride
88		Trichloroethylene
89	$1.703^{\frac{20}{4}}$	Isopropyl iodide
91	1.272^{15}	Isobutyl bromide
98	2.498^{15}	Methylene bromide
98 d.	1.571^{0}	*tert*-Butyl iodide
98	1.166^{14}	Propylene chloride
100	1.279^{20}	*n*-Butyl bromide
100	0.886^{0}	Isoamyl chloride
101	1.848^{12}	Allyl iodide
102	$1.743^{\frac{20}{4}}$	*n*-Propyl iodide
107	1.689^{19}	*s*-Ethylene chlorobromide
108	$1.194^{\frac{25}{25}}$	*tert*-Amyl bromide
112	2.100^{17}	Ethylidene bromide
114	1.457^{10}	1, 2, 2-Trichloroethane
118	1.206^{22}	Isoamyl bromide
119	1.595^{20}	*sec*-Butyl iodide
120	1.608^{19}	Isobutyl iodide
121	1.631^{9}	Tetrachloroethylene
125	$1.189^{\frac{18}{4}}$	Trimethylene chloride
128	1.497^{19}	*tert*-Amyl iodide
130	$2.178^{\frac{20}{4}}$	Ethylene bromide, m. 9°
130	1.613^{20}	*n*-Butyl iodide
132	$1.112^{\frac{15}{15}}$	Chlorobenzene
141–2	0.98^{15}	Chlorocyclohexane
142	1.933^{20}	Propylene bromide
147	1.614^{0}	*s*-Tetrachloroethane
148	1.473^{20}	Isoamyl iodide
151	2.904^{15}	Bromoform, m. 9°
155	1.417^{15}	Glycerol trichlorhydrin
157	1.491^{20}	Bromobenzene
159	$1.081^{\frac{20}{4}}$	*o*-Chlorotoluene
161	$1.693^{\frac{10}{4}}$	Pentachloroethane
162	$1.072^{\frac{20}{4}}$	*m*-Chlorotoluene
162	1.070^{20}	*p*-Chlorotoluene, m. 7°
165	$1.820^{\frac{20}{0}}$	1, 2-Dibromobutane
165	1.973^{17}	Trimethylene bromide

GROUP VI. SUB-GROUPS 3 and 4—*Continued*

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
60°/10 mm.		Bromocyclohexane
172	1.307^{0}	*m*-Dichlorobenzene
174–8	1.133^{16}	*n*-Heptylbromide
179	1.114^{4}	Benzyl chloride
179	1.328^{0}	*o*-Dichlorobenzene
180 d.	3.285^{15}	Methylene iodide, m. 4°
181	$1.422\frac{20}{4}$	*o*-Bromotoluene
183	$1.410\frac{20}{4}$	*m*-Bromotoluene
185	$1.354\frac{64}{4}$	*p*-Bromotoluene, m. 28°
188	1.832^{20}	Iodobenzene
195	1.246^{20}	2, 4-Dichlorotoluene
198	$1.438\frac{22}{0}$	Benzyl bromide
200 d.	$2.971\frac{17}{4}$	*s*-Tetrabromoethane
204	1.698^{20}	*m*-Iodotoluene
211	1.697^{20}	*o*-Iodotoluene
211	——	*p*-Iodotoluene
212	1.295^{16}	Benzal chloride
213	1.380^{14}	Benzotrichloride
214	——	*o*-Chlorobenzyl chloride
214	——	*p*-Chlorobenzyl chloride, m. 29°
110–15/15 mm.	——	*o*-Bromobenzyl chloride
219	$1.955\frac{18}{4}$	*m*-Dibromobenzene
219	2.436^{23}	Glycerol tribromohydrin, m. 16°
220 d.	1.39^{25}	ω-Bromostyrene
224	1.977^{17}	*o*-Dibromobenzene
175–80/45 mm.		Lauryl bromide
263	$1.194\frac{20}{4}$	α-Chloronaphthalene
279	1.488^{17}	α-Bromonaphthalene, m. 4°
200/30 mm.		Diphenyldichloromethane

GROUP VI. SUB-GROUPS 3 and 4

SOLIDS

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
16°	219°	Glycerol tribromohydrin
28	185	*p*-Bromotoluene
35	211	*p*-Iodotoluene
45	184/20 mm.	Diphenylbromomethane
48		*p*-Chlorobenzyl bromide
51	236	*p*-Bromobenzyl chloride
53	172	*p*-Dichlorobenzene
56	266	β-Chloronaphthalene
59	281	β-Bromonaphthalene
67		1, 2-Dibromonaphthalene
81–2		Ethylene iodide
89	219	*p*-Dibromobenzene
92	189 d.	Carbon tetrabromide
106–9		Triphenylchloromethane
116		Iodoform
128		*p*-Diiodobenzene
129	210	Pinene hydrochloride
157		Bornyl chloride
169-70		*s*-Tetramethyl dibromoethane
180		1, 2, 4, 5-Tetrabromobenzene
182		Naphthalene tetrachloride
187		Hexachloroethane
229	326	Hexachlorobenzene

GROUP VII. SUB-GROUP 1

Liquids

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
113°	1.692	Chloropicrin
126	$1.650^{\frac{13}{4}}$	Tetranitromethane, m. 13°
110/40 mm.	1.025^{20}	1-Nitro-1-methylcyclohexane
101–2/10 mm.		2-Nitro-*p*-xylene
209	$1.203^{\frac{20}{4}}$	Nitrobenzene, m. 5°
224	$1.168^{\frac{15}{15}}$	*o*-Nitrotoluene
231	1.168^{22}	*m*-Nitrotoluene, m. 16°
238	1.126^{17}	4-Nitro-*m*-xylene, m. 2°
126–8/10 mm.		2-Nitrocymene
150–1/10 mm.		Methyl-*o*-nitrobenzoate
265	1.268^{20}	*o*-Nitroanisole, m. 9°
268		*o*-Nitrophenetole
275–8 d.		*m*-Nitrobenzoyl chloride, m. 35°
175–80/3 mm.		*m*-Nitrobenzyl alcohol, m. 27°

GROUP VII. SUB-GROUP 1

Solids

MELTING-POINT	BOILING POINT	NAME OF COMPOUND
13°	126°	Tetranitromethane
16	231	*m*-Nitrotoluene
27	175–80/3 mm.	*m*-Nitrobenzyl alcohol
32	246	*o*-Chloronitrobenzene
33–5	275–8 d.	*m*-Nitrobenzoyl chloride
43	261	*o*-Bromonitrobenzene
44	235	*m*-Chloronitrobenzene
44	150/20 mm.	*o*-Nitrobenzaldehyde
44	225	Nitromesitylene
45	173/30 mm.	*m*-Nitrobenzyl chloride
47	296	Ethyl *m*-nitrobenzoate
48		*o*-Nitrobenzyl chloride
49		*o*-Nitroiodobenzene
50	315 d.	Chloro-2, 4-dinitrobenzene
54	258	*p*-Nitroanisole
54	238	*p*-Nitrotoluene
54	266	2, 5-Dichloronitrobenzene

GROUP VII. SUB-GROUP 1—*Continued*

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
56°	256°	*m*-Bromonitrobenzene
58		*m*-Nitrobenzaldehyde
60	304	α-Nitronaphthalene
60	283	*p*-Nitrophenetole
64		*s*-Trinitroanisole
65		*m*-Nitroethylaniline
65		*m*-Nitrobenzal chloride
66		2, 6-Dinitrotoluene
70		2, 4-Dinitrotoluene
71		*p*-Nitrobenzyl chloride
72		Bromo- 2, 4-dinitrobenzene
74		*o*-Nitrobenzyl alcohol
75	202/100 mm.	*p*-Nitrobenzoyl chloride
78		*s*-Trinitrophenetole
78		Methyl *m*-nitrobenzoate
78		β-Nitronaphthalene
80		1-Nitro-1-methylcyclohexane
82		*s*-Trinitrotoluene
83	242	*p*-Chloronitrobenzene
83		Picryl chloride
90	302	*m*-Dinitrobenzene
92		*o*-Nitroacetanilide
92		3, 5-Dinitrotoluene
93		*p*-Nitrobenzyl alcohol
93		4, 6-Dinitro-*m*-xylene
94		3-Nitro-4-acetaminotoluene
96		Methyl *p*-nitrobenzoate
96		Dinitrohydroquinone diacetate
99		*p*-Nitrobenzyl bromide
106		*p*-Nitrobenzaldehyde
116		3-Nitro-4-aminotoluene
116		*p*-Nitrophenylacetonitrile
118		*p*-Nitroethylacetanilide
119		2, 4, 6-Trinitrobenzaldehyde
121		*s*-Trinitrobenzene
126	255	*p*-Bromonitrobenzene
130–2		4–Nitrodiphenylamine
142		*m*-Nitrobenzamide
149–51		*p*-Nitromethylaniline
153		*m*-Nitrobenzanilide
153		*p*-Nitromethylacetanilide

GROUP VII. SUB-GROUP 1—*Continued*

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
154°		*m*-Nitroacetanilide
171		*p*-Nitroiodobenzene
176		*o*-Nitrobenzamide
183		2, 6-Dichloro-4-nitroaniline
183		3, 5-Dinitrobenzamide
201		*p*-Nitrobenzamide
207		*p*-Nitroacetanilide
210		1, 5-Dinitronaphthalene
246–7		Nitroguanidine

GROUP VII. SUB-GROUP 2

SOLIDS

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
	273–5°/718 mm.	Acetyl *n*-butylaniline
38°	298	*N*-Ethyl phenacetin
41	295–300	*N*-Methyl phenacetin
46	284	Formanilide
48	360 d.	Benzoyl piperidine
50	266	Acetyl *n*-propylaniline
51	237 d.	*N*-Phenyl urethane
53–4		*n*-Butyl carbamate
54	300	Benzalaniline
54	258	*N*-Ethyl acetanilide
54	310	Diphenylamine
54–6		Acetyl methyl-*o*-toluidine
60		Isoamyl carbonate
60		Ethyl hippurate
62		*N*-Phenyl-α-naphthylamine
62–4		Isoamyl carbamate
65	303	Acetyl *m*-toluidine
66		Ethyl oxanilate
70		Ethyl-β-naphthyl carbamate
71		*o*-Nitroaniline
72		Diphenyl urethane
73		Formyl diphenylamine
77	262	*s*-Trichloroaniline
79		Ethyl α-naphthyl carbamate
79	330	Di-*p*-tolylamine

GROUP VII. SUB-GROUP 2—*Continued*

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
79°		Diethylcarbanilide
83	283°	Acetyl methyl-*p*-toluidine
85		Acetoacetanilide
86	220 d.	Benzyl carbamate
88		*n*-Butyl oxamate
90		*n*-Butyranilide
92		*o*-Nitroacetanilide
94		3-Nitro-4-acetylaminotoluene
97–8		Diacetyl-*N*-methyl-*p*-aminophenol
98	234	Dichloroacetamide
101		Acetyl diphenylamine
102	260	Methyl acetanilide
103		Propionanilide
109		Isovaleranilide
110		Hydrobenzamide
110–11	296	Acetyl *o*-toluidine
114	305	Acetanilide
114		Ethyl oxamate
116		Diethyl bromoacetyl carbamide
116		3-Nitro-4-aminotoluene
117		3-Bromo-4-acetylaminotoluene
117		α-Phenylacetanilide
117	250 d.	Furfuramide
118		*p*-Nitro-*N*-ethylacetanilide
119	300	*s*-Tribromoaniline
120	350	Dimethylcarbanilide
127	347	Triphenylamine
127		Acetyl *p*-anisidine
128		*s*-Acetyl phenylhydrazine
128	290	Benzamide
128–30		Piperine
129		4-Acetamino-*m*-xylene
132		Aceto-β-naphthylamine
135		Phenacetin
138		2, 6-Dinitroaniline
142		*m*-Nitrobenzamide
142		Cinnamamide
142		Benzo-*o*-toluidine
145		α-Bromo-isovaleryl urea
147		Benzyl carbamide
147		Phenyl carbamide
150		Cinnamanilide

GROUP VII. SUB-GROUP 2—*Continued*

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
151°		Succinanil
153	307°	Acetyl-*p*-toluidine
153		*m*-Nitrobenzanilide
154		*m*-Nitroacetanilide
154	281–4 d.	*α*-Phenylacetamide
155		*o*-Bromobenzamide
155		*m*-Bromobenzamide
158	232	*p*-Benzotoluidide
159		Aceto-*α*-naphthylamine
159–60		*p*-Toluamide
160		Benzanilide
161		Benzoyl-*α*-naphthylamine
166		Phenyl isocyanate
167		*p*-Bromoacetanilide
167		Dibenzylcarbamide
168		Benzoyl phenylhydrazine
168–9		*p*-Acetylaminophenol
173–4		*p*-Phenetyl urea
176		*o*-Nitrobenzamide
179		*p*-Chloroacetanilide
180		2, 4-Dinitroaniline
181–2		*p*-Iodoacetanilide
183		3, 5-Dinitrobenzamide
183		*o*-Iodobenzamide
185		Diacetyl-*o*-phenylenediamine
186		*m*-Iodobenzamide
188		Picramide
189		*p*-Bromobenzamide
190		Biuret
191		Diacetyl-*m*-phenylenediamine
201		*p*-Nitrobenzamide
203–5		Phthalanil
207		*p*-Nitroacetanilide
217		*p*-Iodobenzamide
219 d.		Phthalamide
226		Succinanilide
238	260 subl.	Carbanilide
238–40		*N*-Acetyl-*p*-methylaminophenol
242–3		Succinamide
245–7		Oxanilide
300+		Diacetyl-*p*-phenylenediamine
—— subl.		Oxamide

GROUP VII. SUB-GROUP 3

Liquids

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
107–8°		Isobutyronitrile
118	0.795^{12}	*n*-Butyronitrile
141	0.816^{0}	*n*-Valeronitrile
155	0.806^{20}	Isocapronitrile
170 d.	1.124	Mandelonitrile
191	1.000^{25}	Benzonitrile
205	0.998^{15}	*o*-Toluonitrile
207	1.066	Ethyl cyanoacetate
212	$0.984\frac{25}{25}$	*m*-Toluonitrile
233	$1.017\frac{17}{4}$	Phenyl acetonitrile
254	1.037^{0}	Cinnamonitrile
286	0.995^{15}	Trimethylene cyanide

GROUP VII. SUB-GROUP 3

Solids

MELTING POINT	BOILING-POINT	NAME OF COMPOUND
35°	299°	α-Naphthonitrile
38	217	*p*-Toluonitrile
52	265–7 d.	Succinonitrile
66	306	β-Naphthonitrile
129		Methyleneamine acetonitrile

GROUP VII. SUB-GROUP 4

Liquids

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
17°	0.900^{15}	Ethyl nitrite
44	0.935^{20}	*n*-Propyl nitrite
65	1.217^{15}	Methyl nitrate
67	0.888^{4}	Isobutyl nitrite
75	0.911^{0}	*n*-Butyl nitrite
87	1.116^{15}	Ethyl nitrate
99	0.880^{15}	Isoamyl nitrite
110	1.063^{15}	*n*-Propyl nitrate
123	1.021^{15}	Isobutyl nitrate
130–1	$0.967\frac{21}{4}$	Pyrrol
136	1.048^{0}	*n*-Butyl nitrate
147	1.000^{7}	Isoamyl nitrate
166	0.977^{15}	Phenyl isocyanate
230 d.		Camphorphenylhydrazone

GROUP VII. SUB-GROUP 4

Solids

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
36°		Azoxybenzene
42	165°/90 mm.	Acetone phenylhydrazone
55		*o*-Azotoluene
59		*o*-Azoxytoluene
63		Acetaldehyde phenylhydrazine
66		Diphenyl nitrosoamine
68		Nitrosobenzene
68	296	Azobenzene
70		*p*-Azoxytoluene
93		Benzalazine
96		Diazoaminobenzene
103–5		Acetophenone phenylhydrazone
127	287/205 mm.	1-Phenyl-3-methyl pyrazolon-5
130		Hydrazobenzene
131		*o*-Azophenetole
137		Benzophenone phenylhydrazone
144		*p*-Nitrosodiphenylamine
144		*p*-Azotoluene
154		*pp'*-Dichloroazoxybenzene
156		Benzaldehyde phenylhydrazone
160		*p*-Azophenetole
161		*o*-Hydrazotoluene

GROUP VII. SUB-GROUPS 5 and 6

Liquids

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
36°	$0.839\frac{20}{4}$	Ethyl mercaptan
37	0.845^{21}	Methyl sulfide
46	1.292^{0}	Carbon disulfide
83–4	$1.06\frac{25}{25}$	Thiophene
92-3	$0.837\frac{20}{4}$	Ethyl sulfide
97	0.858^{0}	*n*-Butyl mercaptan
121	$1.046\frac{16}{4}$	Methyl sulfite
133	1.069^{24}	Methyl thiocyanate
140	$0.887\frac{27}{4}$	Allyl sulfide
146	1.007^{24}	Ethyl thiocyanate

GROUP VII. SUB-GROUPS 5 and 6—*Continued*

BOILING-POINT	SPECIFIC GRAVITY	NAME OF COMPOUND
150°	1.006^{24}	Allyl isothiocyanate
153	$0.993^{\frac{20}{4}}$	Ethyl disulfide
161	1.106^{0}	Ethyl sulfite
184–7	0.852	*n*-Butyl sulfide
188	1.333^{15}	Dimethyl sulfate
194	1.058^{20}	Benzyl mercaptan
208	1.184^{19}	Diethyl sulfate
221	1.129^{23}	Phenyl isothiocyanate
231	1.155^{17}	Phenyl thiocyanate
251 d.	$1.384^{\frac{15}{15}}$	Benzenesulfonyl chloride, m. 14°
— d.		*o*-Toluenesulfonyl chloride
292	$1.118^{\frac{15}{15}}$	Diphenyl sulfide

GROUP VII. SUB-GROUPS 5 and 6

SOLIDS

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
14°	251° d.	Benzenesulfonyl chloride
28		Methyl *p*-toluenesulfonate
32	173/15 mm.	Ethyl *p*-toluenesulfonate
35		Phenyl benzenesulfonate
41	230–5 d.	Benzyl thiocyanate
43		*n*-Butyl sulfone
49		Benzyl sulfide
52		Phenyl *o*-toluenesulfonate
52–3		*o*-Cresyl *p*-toluenesulfonate
60	310	Phenyl disulfide
63		Benzene-*m*-disulfonyl chloride
68	194/13 mm.	α-Naphthalenesulfonyl chloride
69	145/15 mm.	*p*-Toluenesulfonyl chloride
70		Phenyl sulfoxide
71		Benzyl disulfide
75		*p*-Bromobenzenesulfonyl chloride
76		Trional
76	201/13 mm.	β-Naphthalenesulfonyl chloride
80		Benzenesulfonylmethylaniline
87		*p*-Toluenesulfonylethylaniline
94		*p*-Toluenesulfonylmethylaniline
94		Phenyl *p*-toluenesulfoate
94–5		*p*-Toluenesulfonylmethylaniline
98		Allyl phenyl thiocarbamide
101	246	α–Trithioacetaldehyde

GROUP VII. SUB-GROUPS 5 and 6—*Continued*

MELTING-POINT	BOILING-POINT	NAME OF COMPOUND
114°	284°	Thiophthalic anhydride
124		Benzenesulfonyldiphenylamine
125	300 d.	Sulfonal
125–6	245–8	β-Trithioacetaldehyde
128	377	Diphenyl sulfone
128		Dibenzenesulfonylaniline
133		Benzyl sulfoxide
150		Dibenzyl sulfone
153		Thiocarbanilide
154		Phenyl thiocarbamide
216 subl.		Trithioformaldehyde

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